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THE PHOTOCHEMICAL REACTIONS OF NAPHTHALENE
WITH DIMETHYL ACETYLENEDICARBOXYLATE

A THESIS

Presented to
The Faculty of the Graduate Division
by

Thomas Cooper Campbell

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THE PHOTOCHEMICAL REACTIONS OF NAPHTHALENE

WITH DIMETHYL ACETYLENEDICARBOXYLATE

Approved:

Chairman

Date approved by Chairman: Sept. 5, 1967

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SUMMARY

The purpose of this research was to study the photochemical reaction of dimethyl acetylenedicarboxylate (DMAD) with naphthalene under varying conditions of solvent and temperature. The reactants were irradiated at room temperature in methanol, cyclohexane, and benzene, and in methanol at 65°. Also DMAD was irradiated in molten naphthalene at 95°. The thermal reaction of naphthalene with DMAD was carried out at 95° and 180° in a sealed tube.

Six compounds corresponding to 1:1 adducts of naphthalene and DMAD were observed in the various reaction mixtures in different amounts. The major compounds isolated were dimethyl 1-naphthylfumarate, 1, dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate, 2, and dimethyl trans-acenaphthene-1,8-dicarboxylate, 3. The minor products which were shown to be present by vpc analysis but not isolated from the reaction mixtures, were dimethyl 2,3-benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate, 4, and dimethyl 1,2-benzocyclooctatetraene-5,6-dicarboxylate, 5. The sixth 1:1 adduct was not isolated or identified.

Poor yields of 1:1 adducts were obtained when dilute solutions of naphthalene and DMAD were photolyzed at room temperature in methanol, cyclohexane, or benzene. In each case the solvent reacted photochemically with the DMAD to form 1:1 adducts. In methanol dimethyl 2-hydroxymethylfumarate was formed. In cyclohexane, two cyclohexyl adducts, apparently dimethyl cyclohexylfumarate and dimethyl cyclohexylmaleate, were formed. In benzene, dimethyl cyclooctatetraene-1,2-dicarboxylate was

formed in poor yield. The photolysis of a more concentrated solution of naphthalene and DMAD in methanol at reflux gave nearly a 10 percent yield of 1:1 adducts with the major product being 3, which was isolated from this reaction mixture.

The photolysis of DMAD in molten naphthalene at 95° gave 10-12 percent of 1:1 adducts with 1 and 2 being the major products. Compound 3 was also formed in an appreciable amount. Two minor products, 4 and 5, were shown to be present by vpc retention times.

The thermal reaction of naphthalene with DMAD in a sealed tube at 180° gave 4 as the major isolated product in 17-23 percent yields. Photolysis of 4 in methanol gave 5 in yields up to 80 percent. Compounds 4 and 5 were identified from their spectral and chemical properties. Compound 4 was hydrogenated to form a known compound, dimethyl 2,3-benzobicyclo[2.2.2]octane-exo-5,6-dicarboxylate.

Compound 1 was identified from its spectral and chemical properties. It was hydrogenated to give a dihydro compound, dimethyl 1-naphthylsuccinate, which was identical to the compound formed by hydrogenation of dimethyl 1-naphthylmaleate which had been synthesized by a known procedure. Irradiation of 1 and dimethyl 1-naphthylmaleate in dilute methanol solutions produced 3 in good yields. Compounds 2 and 3 were identified from their spectral and chemical properties.

The photochemical reactions of DMAD with naphthalene apparently follow different paths than other reactions of this type since no products arising from 1,2-cycloaddition reactions were observed. The products isolated from the reaction came from either photochemical 1,3-cycloaddition, thermal 1,4-cycloaddition, or bond formation of the acetylene moiety at

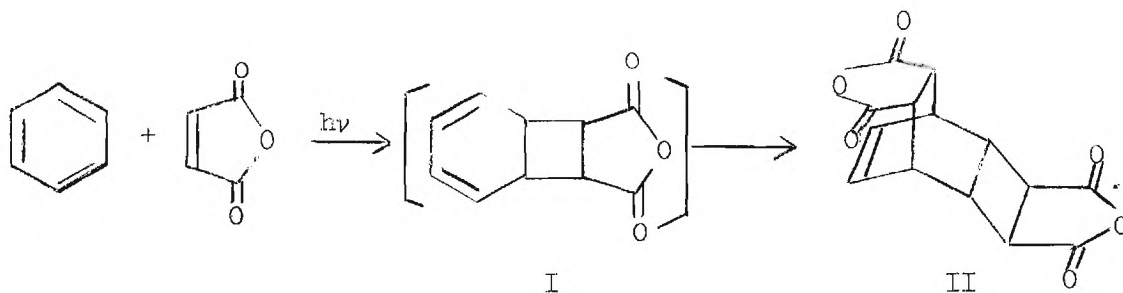
the 1-position of the electronically excited naphthalene followed by a 1,3-proton transfer to give a vinylnaphthalene derivative which could then undergo further photolysis to form an acenaphthene derivative. The photochemical reaction of 4 in methanol was unusual in that it gave 5 as a major product rather than benzo[3.3.0.^{2,8}octa-3,6-diene derivatives, which would have been the products predicted from other work with similar compounds. The facile photochemical ring closure reactions of 1 and dimethyl 1-naphthylmaleate to give the same product, 3, in good yields was unexpected since this type of reaction had been reported in only one other case in poor yield.

CHAPTER I

INTRODUCTION

The purpose of this research was to study the reaction of naphthalene with dimethyl acetylenedicarboxylate activated by ultraviolet radiation. The structures of the compounds formed were determined and the influence of varying reaction conditions upon the amounts of reaction products was studied. This work is a natural sequel to the study of the photochemical reactions of benzene with maleic anhydride^{1,2} and the dimethyl acetylenedicarboxylate.^{3,4}

Benzene reacts photochemically with maleic anhydride apparently to form the 1,2-cycloadduct, I, which in turn reacts further with maleic anhydride to form the final 2:1 adduct, II, which has the stereochemistry shown.¹



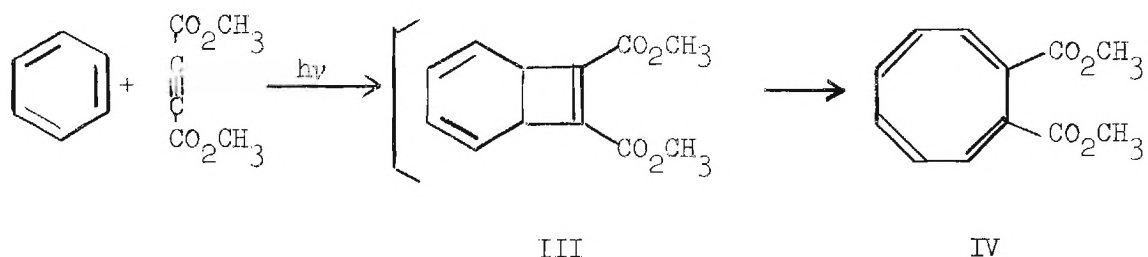
1. E. Grovenstein, Jr., D. V. Rao, and J. W. Taylor, J. Am. Chem. Soc., **83**, 1705 (1961).

2. H. J. F. Angus and D. Bryce-Smith, J. Chem. Soc., 4791 (1960).

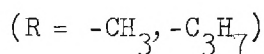
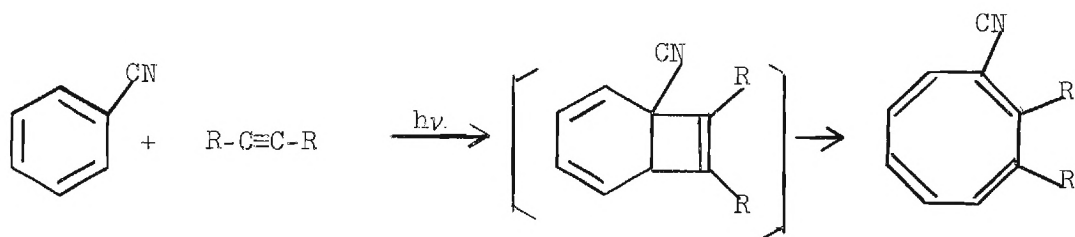
3. E. Grovenstein, Jr. and D. V. Rao, Tetrahedron Letters, 148 (1961).

4. D. Bryce-Smith and J. E. Lodge, J. Chem. Soc., 695 (1963).

The reaction of benzene with dimethyl acetylenedicarboxylate in the presence of ultraviolet light probably yields the 1,2-cycloadduct, III, initially, but before the adduct can react further it tautomerizes to form dimethyl cyclooctatetraene-1,2-dicarboxylate, IV.^{3,4} Benzene also reacts with methyl propiolate and phenylacetylene photochemically to form 1:1 adducts similar to IV.⁴

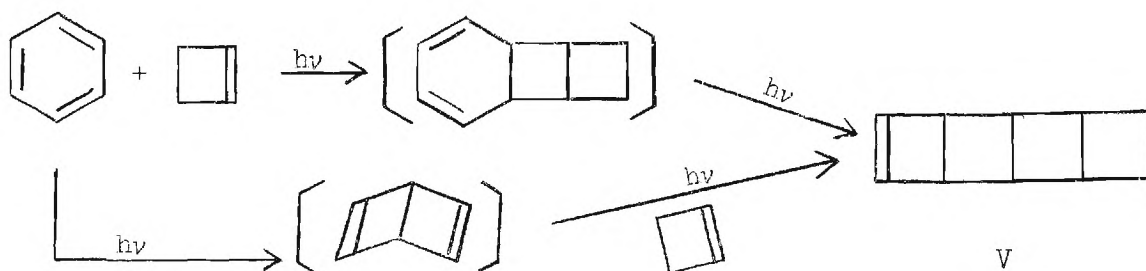


Atkinson, Ayer, Büchi, and Robb⁵ have shown that benzonitrile reacts photochemically with dialkylacetylenes to form 1-cyano-2,3-dialkylcyclooctatetraene derivatives as shown below.



5. J. G. Atkinson, D. E. Ayer, G. Büchi, and E. W. Robb, J. Am. Chem. Soc., 85, 2257 (1963).

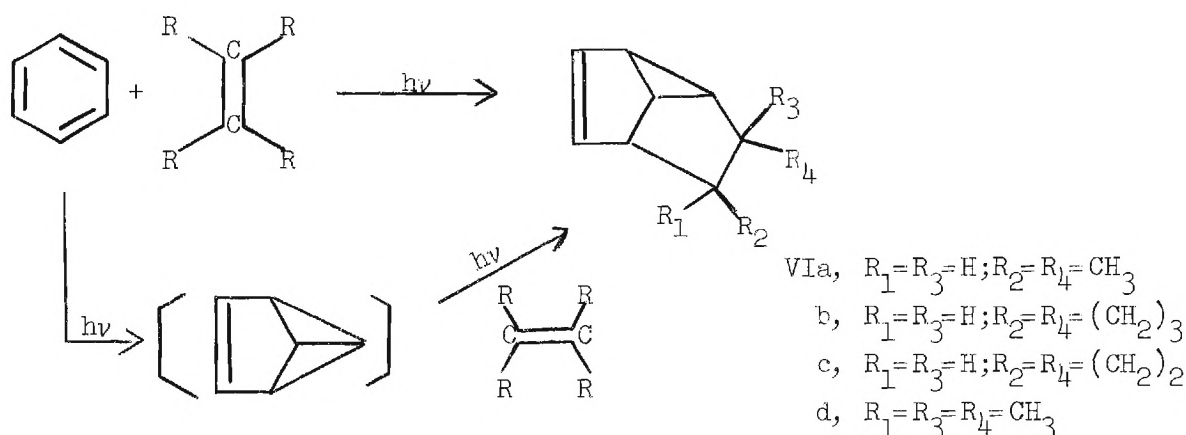
Srinivasan and Hill⁶ found a quadricyclic 1:1 adduct, V, is formed when a 20 percent by volume solution of cyclobutene in benzene is photolyzed at 2537 Å at room temperature. The authors suggested that the reaction may have proceeded via a "Dewar" benzene intermediate or by 1,2-cycloaddition followed by an internal cyclization as shown below.



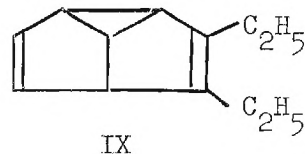
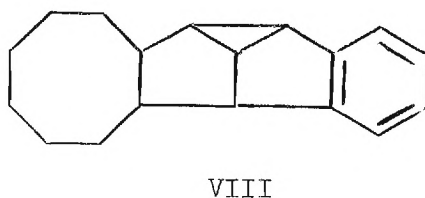
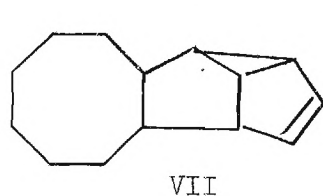
Conversely, Wilzbach and Kaplan⁷ irradiated 10 percent solutions of cis-2-butene, cyclopentene and 2,3-dimethyl-2-butene in benzene at 2537 Å and obtained adducts VI(a,b,c,d) corresponding to 1,3-cycloaddition to benzene via a benzvalene intermediate. The authors reported also that, in a private communication, Dr. R. Srinivasan informed them that he had found a second product in the reaction of benzene with cyclobutene which corresponded to a 1,3-adduct.

6. R. Srinivasan and K. A. Hill, J. Am. Chem. Soc., 87, 4653 (1965).

7. K. E. Wilzbach and L. Kaplan, J. Am. Chem. Soc., 88, 2066 (1966).



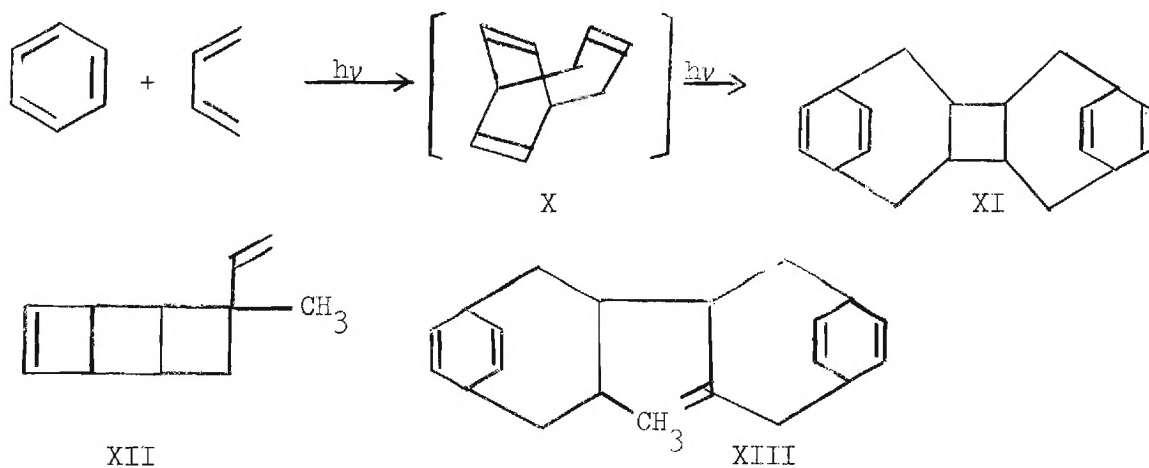
Bryce-Smith, Gilbert, and Orger⁸ reported that they obtained similar 1,3-cycloadducts by irradiating equimolar solutions of cyclooctene, 1-butene, 1-octene, cyclohexene, 1,5-cyclooctadiene, and ethyl vinyl ether in benzene at room temperature with ultraviolet radiation of wavelength 235-285 mμ. The photolysis of cyclooctene and benzene produced a 1:1 adduct in 85 percent yield for which they assigned structure VII from its chemical and spectral characteristics. They also found that naphthalene reacts photochemically with cyclooctene to form two 1:1 photoadducts for which they assign structure VIII to the major isomer from spectroscopic evidence.



8. D. Bryce-Smith, A. Gilbert, and B. H. Orger, Chem. Comm., 512 (1966).

Finally, they report that a 1:1 adduct of probable structure IX was formed when 3-hexyne was irradiated in benzene.

Koltzenburg and Kraft⁹ found that conjugated dienes such as 1,3-butadiene or 2-methyl-1,3-butadiene can undergo photochemically activated addition with benzene or benzene derivatives to give 2:2 adducts as the major products. They postulate that the diene initially adds across the 1,4-positions of the benzene ring to give an intermediate such as X for benzene and 1,3-butadiene, which reacts further to form the 2:2 adduct, XI, as shown below. They also reported that a mixture of 1:1 adducts, XII, and a 2:2 adduct, XIII, was formed from the photolysis of 2-methyl-1,3-butadiene and benzene.

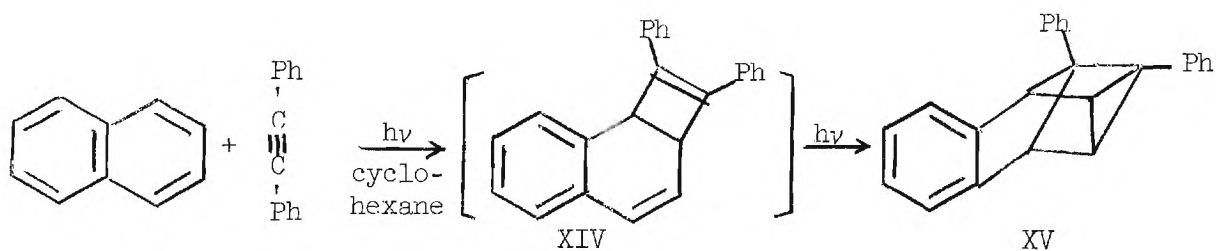


In a work which closely parallels the work covered in this thesis, Sasse, Collins, and Sugowdz¹⁰ reported the photo-addition of diphenyl-

9. G. Koltzenburg and K. Kraft, Tetrahedron Letters, 389 (1966).

10. W. H. F. Sasse, P. J. Collins, and G. Sugowdz, Tetrahedron Letters, 3373 (1965).

acetylene to naphthalene in cyclohexane as a solvent. They found that irradiation of naphthalene and diphenylacetylene for 120 hours with a Pyrex-jacketed 125 watt mercury lamp gave in 29 percent yield a hydrocarbon, $C_{24}H_{18}$, for which they postulated structure XV via the intermediate XIV as shown below.

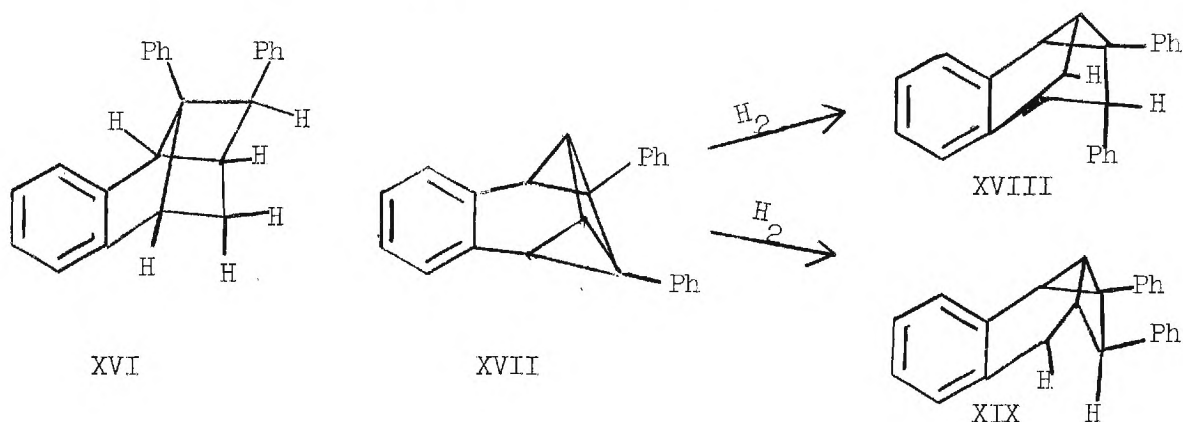


Photoadducts similar to XV were obtained when diphenylacetylene was irradiated with 1,4-, 2,3-, 2,6-, and 2,7-dimethylnaphthalene in cyclohexane. With 1,4- and 2,3-dimethylnaphthalene, the diphenylacetylene added preferentially to the ring which contained the methyl groups.

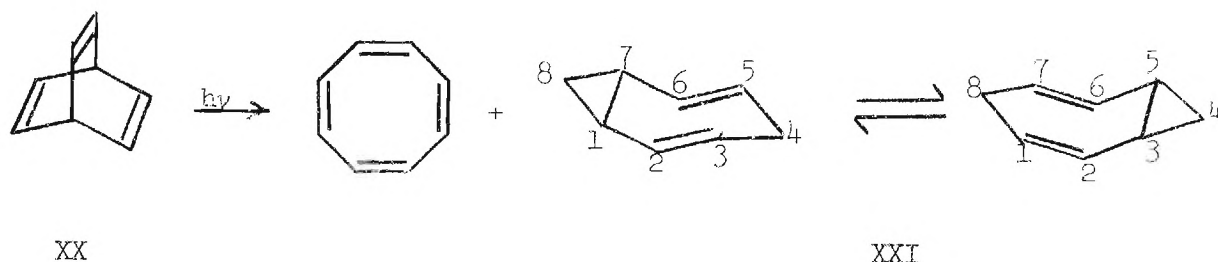
The structure of XV was determined from its chemical behavior and spectral characteristics. The mass spectrum indicated a molecular weight of 306 with the only other relatively intense peaks being at m/e 178 (diphenylacetylene) and m/e 128 (naphthalene). This simple mass spectrum ruled out the possibility of rearrangements of the carbon skeletons of the components during irradiation. The ultraviolet spectrum showed a maximum at $274\text{ m}\mu$ ($\epsilon = 2,300$) with a point of inflexion at $235\text{ m}\mu$ ($\epsilon = 13,000$) and a shoulder at $225\text{ m}\mu$ ($\epsilon = 19,000$) which ruled out the presence of a stilbene-like arrangement of two of the benzene rings in XV. Compound XV was recovered intact after treatment with excess potassium permanganate in boiling acetone for 40 hours, which indicated that the adduct was satu-

rated. The pmr spectrum of XV shows a 14-proton multiplet in the 2.8 to 3.2 τ aromatic region and two 2-proton quartets centered at 5.76 τ and 7.48 τ , respectively. The non-aromatic protons exhibited a symmetrical A_2X_2 pattern with coupling constants of 0.3 and 1.4 cps measured from the center of each quartet. The chemical shift variation of the two cyclopropane protons is probably due to the ring current of the benzene ring. The infrared spectrum was consistent with the postulated structure.

Hydrogenation of XV in the presence of five percent palladium on carbon at atmospheric pressure and room temperature resulted in a single dihydro-derivative, XVI, in better than 90 percent yield. The ultraviolet spectrum of XVI showed only minor changes, while the pmr spectrum showed that the six non-aromatic protons were non-equivalent. These data allowed the authors to postulate structure XV for the adduct rather than structure XVII which could give two dihydro-derivatives, XVIII and XIX. Further evidence for the assigned structure of XV came from the fact that the XVI would not react further with hydrogen even under forcing conditions, whereas both XVIII and XIX contain another labile cyclopropane ring which should readily reduce under the reaction conditions.



Zimmerman and Grunwald¹¹ recently reported on the photoisomerization of bicyclo[2.2.2]octa-2,5,7-triene, XX, to tricyclo[3.3.0.0^{2,8}]octa-3,6-diene, XXI, and a small amount of cyclooctatetraene as shown below.

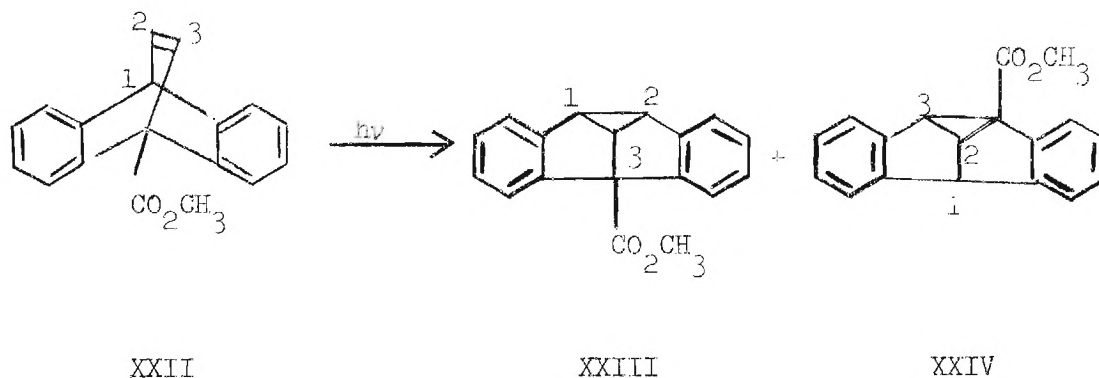


Compound XXI had a pmr spectrum which showed only three varieties of hydrogens in a ratio of 2:4:2. This pattern arises from the rapid equilibrium of the compound with its valence bond tautomer which allows protons 1, 3, 5, and 7 to become equivalent. Protons 4 and 8 also become equivalent while protons 2 and 6 remain unchanged and equivalent. Cooling the compound to -110°C produced no change in the spectrum.

A similar type of photoisomerization was demonstrated by Ciganek¹² who found that several dibenzobicyclo[2.2.2]octatrienes were converted into dibenzotricyclo[3.3.0.0^{2,8}]octadienes. For example, the photolysis of 1-methoxycarbonyl dibenzobicyclo[2.2.2]octatriene, XXII, gave two products, XXIII and XXIV, in a 2:1 ratio as shown.

11. H. E. Zimmerman and G. L. Grunewald, J. Am. Chem. Soc., 88, 183 (1966).

12. E. Ciganek, J. Am. Chem. Soc., 88, 2882 (1966).



The pmr spectrum of XXIII showed eight aromatic hydrogens at 2.4 to 3.1 τ , a one hydrogen triplet centered at 5.96 ($J = 6.5$ cps), a three hydrogen singlet at 6.20 τ , and a two hydrogen doublet centered at 6.92 τ ($J = 6.5$ cps). The pmr spectrum of XXIV showed eight aromatic hydrogens at 2.1 - 3.2 τ , a one hydrogen doublet centered at 5.50 τ ($J = 5.0$ cps), two hydrogens in a multiplet extending from 5.9 to 6.1 τ , and a three hydrogen singlet at 6.23 τ . The chemical shifts shown by the non-aromatic bridgehead hydrogens in the above compounds are somewhat unusual in that they absorb at a much lower field than would be predicted a priori. In compound XXIII, the cyclopropane hydrogen at position 3 absorbs at 5.96 τ which is quite removed from what would be expected for a proton on a cyclopropane ring which is also two carbon atoms removed from an electron-rich phenyl- or carboxyl- group. Evidently the ring-current from the two benzene rings and the proximity of the carbonyl group cause the unexpected chemical shift for this proton. A similar effect is operating on proton two in XXIV.

CHAPTER II

REAGENTS AND SOLVENTS

Acetic Acid, Glacial

Baker reagent grade acetic acid was used without further purification.

Acetic Anhydride

Eastman white label grade acetic anhydride was redistilled at 140°C through a 15 cm Vigreux column.

Acetone

Commercial grade acetone was distilled through a 30 cm Vigreux column, followed by distillation from potassium permanganate and potassium carbonate through a 15 cm Vigreux column.

Alumina

Merck acid washed alumina was used without further treatment.

1-Aminonaphthalene

Eastman technical grade 1-aminonaphthalene was treated with decolorizing charcoal and recrystallized from 95 percent ethanol to give pink crystals melting at 47-48°C.

2-Aminonaphthalene

Aldrich reagent grade 2-aminonaphthalene was used without further purification.

Benzene

Matheson, Coleman & Bell, Inc., industrial grade (thiophene-free) benzene was distilled through a 30 cm column packed with glass helices.

Benzylamine

Eastman yellow label benzylamine was used without further purification.

Carbon Tetrachloride

Baker spectroscopic grade carbon tetrachloride was used without further purification.

Chloroform

Baker reagent grade chloroform was used without further purification.

Cyclohexane

Phillips 99.5 percent cyclohexane was purified by passing one liter through an alumina column of dimensions 2.0 by 30 cm containing 150 g of alumina. The first 100 ml and last 200 ml were discarded.

Deuteriochloroform

Volk 99.7 percent deuteriochloroform was used without further purification.

Diazomethane in Ether

A solution of diazomethane in ether was prepared by the method of

de Boer and Backer.¹³ A solution of 21.5 g (0.1 mole) of N-methyl-N-nitroso-p-toluenesulfonamide in 130 ml of ether was added dropwise to a solution of 5.0 g of KOH (0.09 mole) in 8.0 ml of water and 25 ml of 95 percent ethanol at 65°C. The diazomethane codistilled with the ether and the resulting solution was stored in the freezer until needed.

Diethyl Ether

Baker reagent grade diethyl ether was used without further purification.

Dimethyl Acetylenedicarboxylate

Aldrich reagent grade dimethyl acetylenedicarboxylate was redistilled at 92-93°C at 15 mm pressure through a 15 cm Vigreux column.

Dimethyl Cyclooctatetraene-1,2-dicarboxylate

A sample prepared by Grovenstein and Rao³ was used without further purification.

Ethanol

Commercial absolute ethanol was distilled from magnesium through a 30 cm column packed with glass helices. Commercial 95 percent ethanol was used without further purification.

Ethyl Acetate

Commercial ethyl acetate was distilled through a 30 cm column packed with glass helices

13. T. J. de Boer and H. J. Backer, Rec. trav. chim., 73, 229 (1954).

Lead Tetraacetate

Eastman white label lead tetraacetate was recrystallized from glacial acetic acid and stored in a vacuum dessicator.

Maleic Acid

Eastman technical grade maleic acid was recrystallized from acetone after treatment with decolorizing charcoal to give white crystals melting at 130-131°C.

Methanol

Matheson, Coleman & Bell commercial grade methanol was refluxed over magnesium turnings overnight and then distilled through a 30 cm column packed with glass helices.

Methanol-d₁

Methanol-d₁, generously supplied by Dr. E. C. Ashby, was used without further purification. The isotopic purity was 99 percent.

Methylene Chloride

Eastman white label methylene chloride was used without further purification.

N-Methyl-N-nitroso-p-toluenesulfonamide

Aldrich reagent grade N-methyl-N-nitroso-p-toluenesulfonamide was used without further purification.

Naphthalene

Baker reagent grade naphthalene was used without further purification.

Petroleum Ether

Commercial petroleum ether (b.p. 30°-60°C) was used without further purification.

2-Propanol

Commercial 2-propanol was distilled from magnesium through a 30 cm column packed with glass helices.

Pyridine

Eastman white label pyridine was refluxed for 18 hours over potassium hydroxide pellets and was distilled at 115°C through a 20 cm Vigreux column.

Silica Gel

Brinkman Instruments Company No. 773⁴ silica gel (0.05 to 0.20 mm) was used without further treatment.

Sodium Methoxide

Fisher purified sodium methoxide was used without further purification.

Toluene

Fisher reagent grade toluene was distilled at 110°C through a 30 cm column packed with glass helices.

CHAPTER III

EQUIPMENT AND GENERAL EXPERIMENTAL PROCEDURES

Equipment

Melting points were determined in capillary tubes on a Mel-Temp apparatus. Proton magnetic resonance spectra were obtained at 60 Mc using a Varian Associates Model A-60A spectrometer equipped with a spin-decoupler and variable temperature probe. Ultraviolet and visible spectra were determined on a Cary Model 14 recording spectrophotometer. Infrared spectra were measured on a Perkin-Elmer Model 237 Infracord.

General Experimental Procedures

Analyses

Elemental analyses and molecular weight determinations were performed by Galbraith Laboratories, Knoxville, Tennessee.

Vapor Phase Chromatography

An F & M Scientific Company Model 810 research chromatograph, equipped with dual flame ionization and thermal conductivity detectors, was used for all vapor phase chromatography analyses. A pair of 12 foot, one-fourth inch o.d. stainless steel columns packed with 10 percent SE-30 silicone gum rubber on 80-100 mesh Diatoport S, which had been acid-washed and treated with dichlorodimethylsilane, was used exclusively with the thermal conductivity detectors. Typical operating conditions for using the SE-30 columns on the temperature-programming mode (for analysis

of the photoproducts of naphthalene and DMAD) consisted of holding the oven temperature at 200°C for four minutes, raising the temperature at a constant heating rate of 10° per minute to 325°C, and holding the temperature at 325°C for 10 minutes. The injector port temperature was 300°C and the detector temperature was 350°C. The flow rate as measured by a soap-bubble flowmeter was 100 ml per minute.

A pair of five foot, one-fourth inch o.d. stainless steel columns packed with 10 percent Apiezon L on 60-80 mesh Chromosorp P, which had been acid washed and treated with dichlorodimethylsilane, was used with the flame ionization detectors. Typical operating conditions for these columns with the flame detector for analysis of the photoproducts of naphthalene and DMAD included holding the temperature of the oven constant at 290°C. The flow rate cannot be measured directly due to the design of the instrument, so flow rates were reproduced as closely as possible using the flowmeter and the regulator pressure gauge. In most cases, the flow rate was set at a scale reading of 20 mm at 60 psig, which corresponded to a flow rate of about 50 ml per minute according to the calibration curve supplied with the instrument. The injector port temperature was 300°C and the detector temperature was 370°C.

Liquid Chromatography

All liquid chromatography was done with Brinkman Instruments Company No. 7734 silica gel which had a particle size of 0.05 to 0.20 mm. The columns were fabricated from Pyrex tubing with a fritted disc and a Teflon stopcock at the bottom. The dimensions of the packed columns were usually a ratio of 20:1 to 30:1 of height of the column packing to the diameter. The ratio of silica gel to the sample used for a separation

varied from 50:1 to 100:1 on a weight to weight basis. The columns were packed by filling the column with petroleum ether almost to the top of the column. The desired weight of silica gel was placed in a separatory funnel with a Teflon stopcock. The silica gel was added at a slow, even rate and the stopcock was opened slightly at the bottom of the column so that the liquid level in the column remained nearly constant. The side of the column was tapped gently periodically to keep the silica gel evenly packed. After all of the silica gel had been added to the column, a one inch layer of sea sand was gently poured on top of the silica gel.

The procedure for adding the sample to the column involved dissolving the sample in a minimum amount of a good solvent like chloroform or methylene chloride, pipetting the solution carefully onto the sand layer as evenly as possible, and washing the sand layer with a few milliliters of the solvent. The chloroform or methylene chloride was eluted from the column with petroleum ether prior to addition of the solvent for elution of the sample. Even with careful addition of the sample to the column, the sample tended to elute from the column unevenly.

The easiest method of obtaining fractions was to take samples of 100 ml to one liter in volume depending upon the size of the column. The solvent was removed on the spin evaporator and the residue was washed into tared beakers. Usually the fraction could be analyzed by vpc before the next fraction had finished eluting. The most convenient method for adding the eluting solvent to the top of the column was to fill a large separatory funnel with the eluting solvent and place the funnel stem in the liquid. The separatory funnel was capped with a greased stopper and the stopcock was opened. This method kept a constant head on the column

and increased the rate of flow.

Hydrogenations

All hydrogenations were carried out in an atmospheric pressure apparatus using five percent palladium on charcoal as the catalyst. The catalyst and solvent were prereduced for one to three hours to equilibrate the system. The amount of hydrogen taken up was measured versus time. The temperature and atmospheric pressure were recorded for conversion of the volume of hydrogen to standard conditions.

Photolysis Apparatus and Procedures

The photolyses were carried out in a cylindrical quartz cell which had an inner jacket for temperature control and an outer sample jacket of 350 ml capacity. The temperature of the cell could be varied from 15° to 95°C by passing water through the jacket either from the cold water tap or from a thermostated hot water bath. Nitrogen was bubbled through the solution for all of the photolyses carried out in dilute solutions. Nitrogen could not be bubbled through the cell for the molten naphthalene or refluxing methanol runs due to plugging of the nitrogen inlet. The irradiation apparatus was made by the Hanovia Chemical and Manufacturing Company of Newark, New Jersey, and contained a high pressure mercury lamp (type LL) of 30 cm arc length. The lamp operated on about 1000 watts at a current of 3.8 to 4.2 amperes. A Pyrex filter could be inserted between the lamp and the cell to eliminate nearly all of the radiation below 3000 Å, if so desired.

CHAPTER IV

PHOTOCHEMICAL REACTIONS, SYNTHESSES, AND PRODUCT IDENTIFICATION

Photolysis of Naphthalene and DimethylAcetylenedicarboxylate in SolutionMethanol

A stock solution of 200 g of naphthalene was made up to a volume of 3250 ml with dry methanol and stored in a brown one gallon bottle. For each photolysis, 325 ml of this solution containing 20.0 g of naphthalene (0.156 mole) was poured into the quartz cell. To this solution was added 5.00 ml (5.71 g, 0.040 mole) of dimethyl acetylenedicarboxylate (DMAD). The reaction mixture was irradiated for 24 hours at 15°C with a slow stream of nitrogen passing through the solution. The solution from the irradiation was washed into a one liter round-bottomed flask, and the solvent was removed in vacuo on the rotary evaporator using the water aspirator. A vacuum pump was then attached to the rotary evaporator and the starting materials were removed at 100°C and 0.1 mm. This procedure was repeated nine more times to yield a total of 14.91 g of non-volatile residue. Analysis of the residue by vpc showed that the yield of 1:1 photoadducts of naphthalene and DMAD was as follows: 0.375 g of dimethyl 1-naphthylfumarate (0.32 percent), 0.112 g of dimethyl 3,4-benzotricyclo-[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate (0.10 percent), 0.960 g of dimethyl trans-acenaphthene-1,8-dicarboxylate (0.89 percent), and 0.300 g of unknown adduct (0.29 percent). The yield percentages are based upon

0.400 mole of DMAD used. A separate vpc analysis showed that 1.985 g of dimethyl 2-hydroxymethylfumarate (3.14 percent) had also been formed in the reaction.

A 4.52 g portion of the residue was dissolved in 10 ml of chloroform and added to a 3.4 cm by 66 cm column of Brinkman No. 7734 silica gel containing 255 g of packing. The chloroform was eluted with 500 ml of 30°-60° petroleum ether. The column was eluted with 1500 ml of benzene to give 0.050 g of unknown product which was discarded. Elution with 500 ml of five percent acetone in benzene gave 0.61 g of a mixture of 1:1 adducts; 500 ml more of five percent acetone in benzene gave 1.74 g of a mixture of 1:1 adducts. Elution with 500 ml of 10 percent acetone in benzene gave 0.76 g of a mixture of unknown compounds. Elution with 500 ml of 25 percent acetone in benzene gave 0.72 g of oil which was greater than 90 percent one compound as shown by vpc analysis. Further elution with 500 ml of acetone followed by 500 ml of methanol gave 0.29 g of high molecular weight residue.

The 0.72 g of oil which had been eluted with 25 percent acetone in benzene was dissolved in five ml of chloroform and added to a column containing 65 g of Brinkman No. 7734 silica gel. The column was eluted with 200 ml portions of 10 percent acetone in benzene. The first two fractions were discarded. The third fraction weighed 0.49 g and was shown to be greater than 99 percent one compound having a retention time of 5.6 minutes on the SE-30 column. Further elution with 200 ml of 20 percent acetone in benzene yielded 0.12 g more of the compound in 92 percent purity. The colorless oil had a pmr spectrum which showed 1.0 proton at 3.78 τ (triplet, $J = 1.8$ cps), 2.01 protons at 5.70 τ (doublet,

$J = 1.8$ cps), 3.10 protons at 6.22 τ (singlet), and 3.12 protons at 6.30 τ (singlet). The infrared spectrum had the following absorptions: 2.75 μ to 3.2 μ (broad, -OH), 5.78 μ (strong, C = O), 6.00 μ (medium, C = C). The pmr and infrared spectra were consistent with the assignment of dimethyl 2-hydroxymethylfumarate for the compound. The compound was not investigated further since it arose from the photochemical addition of methanol to DMAD analogous to the photochemical addition of 2-propanol to acetylene dicarboxylic acid.¹⁴

In order to improve the yield of photo-products from this reaction, the photolysis apparatus was modified so that a condenser could be attached to the upper opening of the quartz cell. Hot water at 65°-68°C was passed through the water-jacket of the quartz cell from the hot water tap. A solution of 60 g (0.47 mole) of naphthalene and 20 ml (22.8 g, 0.16 mole) of DMAD in 275 ml of hot methanol was added to the quartz cell. The cell was placed in the photolysis apparatus and the mercury lamp was turned on. The hot water flow was adjusted so that the solution in the cell refluxed very gently. The mixture was irradiated for 60 hours. The solution from the cell was poured into a flask; the cell was rinsed with acetone and methanol, and the reaction was repeated using the same amounts of materials. The solvent and starting materials were removed from the combined reaction mixtures in vacuo to give 54.1 g of non-volatile residue. The residue was dissolved in 50 ml of chloroform. The solution was poured slowly into three liters of 30°-60° petroleum ether. The precipitate was removed by filtration and dried to give 29.1 g of insoluble resi-

14. G. O. Schenck and R. Steinmetz, Natur., 47, 514 (1960).

due, which was discarded. The solvent was removed from the filtrate in vacuo to give 24.3 g of petroleum ether soluble residue.

Analysis of the residue by vpc indicated that the reaction yielded 0.682 g of dimethyl 1-naphthylfumarate (0.79 percent), 0.614 g of dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate (0.71 percent), 6.46 g of dimethyl trans-acenaphthene-1,8-dicarboxylate (7.46 percent), and 0.753 g of unknown adduct (0.81 percent). Less than 0.050 g of other 1:1 adducts were formed. The yield percentages are based upon the amount of DMAD used.

The residue was dissolved in 30 ml of chloroform and added to a column packed with 1945 g of Brinkman No. 7734 silica gel with packing dimensions of 6.5 cm by 130 cm. The chloroform was eluted with 500 ml of 30°-60° petroleum ether. Elution of the column with four liters of three percent ethyl ether in benzene gave 0.18 g of unknown product which was discarded. Elution with two liters of five percent ethyl ether in benzene followed by two one-liter portions of the same solvent gave three fractions weighing 1.96 g, 2.64 g, and 3.88 g, respectively, which contained all of the 1:1 adducts. Further elution with two liters of the same solvent yielded 4.72 g of unknown compounds. The fractions containing the 1:1 adducts were combined and dissolved in 25 ml of boiling methanol. The solution was cooled in the refrigerator overnight. White crystals, melting at 84.0°-85.0° and weighing 6.13 g, were recovered by filtration. Recrystallization from methanol did not change the melting point. The compound isolated was dimethyl acenaphthene-trans-1,8-dicarboxylate. The isolated yield was 7.06 percent based on DMAD used.

Cyclohexane

A solution of 20.0 g of naphthalene (0.156 mole) and 5.0 ml of DMAD (0.040 mole) in 325 ml of cyclohexane was irradiated in the quartz cell under nitrogen for 24 hours. The solvent and starting materials were removed in vacuo to give 1.332 g of non-volatile residue. Analysis of the residue by vpc showed that the solvent had reacted with the DMAD and it was estimated from the vpc trace that less than five percent by weight of 1:1 adducts was present in the residue.

To 300 ml of cyclohexane in the quartz cell was added 8.0 ml of DMAD (0.064 mole). The solution was irradiated under nitrogen for 24 hours. An insoluble polymer had formed in the cell during the photolysis. The polymer was removed by filtration and dried. It weighed 3.55 g. The filtrate was evaporated on the spin evaporator using the water aspirator to give 7.92 g of viscous yellow liquid. Analysis of the liquid by vpc showed that it contained unreacted DMAD. The liquid was placed in a modified Hickman short-path distillation apparatus heated by a copper block. The liquid was distilled at 20 mm to give 1.02 g of colorless liquid boiling at 110°-120° and 1.52 g of liquid boiling at 150°-160°. The first fraction was mostly DMAD. The second fraction was a mixture of two isomers having retention times of 9.4 minutes and 10.0 minutes on the SE-30 column. The pot-residue did not distill. The two cyclohexane adducts were partially separated by preparative vpc using a six foot, one-half inch polyphenyl ether column operated at 200° with a flow rate of 50 ml per minute. A fraction, weighing 0.76 g, which was 95 percent one compound was isolated by this method. The pmr spectrum showed 0.84 proton at 4.70 τ , 3.0 protons at 6.56 τ , 3.0 protons at 6.67 τ , and 11.5 protons at 7.50 τ .

to 9.2 τ . The compound was assumed to be dimethyl 2-cyclohexylfumarate or dimethyl 2-cyclohexylmaleate.

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.71; H, 7.96; mol. wt. 226

Found: C, 63.00, 63.18; H, 7.85, 7.96; mol. wt., 241, 242

Benzene

A solution of 20 g of naphthalene (0.156 mole) and 5.0 ml of DMAD (0.040 mole) in 325 ml of purified benzene was irradiated in the quartz cell for 22 hours under nitrogen. The solvent and starting materials were removed in vacuo on the rotating evaporator to give 1.01 g of non-volatile residue. Qualitative analysis of the residue by vpc indicated that the DMAD had reacted preferentially with the benzene. Less than 10 percent by weight of 1:1 naphthalene-DMAD photoadducts was estimated to have been formed.

In a separate experiment, the photolysis of 5.0 ml of DMAD (0.040 mole) in 325 ml of benzene for 24 hours in the quartz cell under nitrogen gave 6.46 g of residue after removal of the starting materials in vacuo. Analysis of the residue by vpc indicated that the area of the peak at 9.8 minutes on the SE-30 column corresponded to a weight of 1.33 g of dimethyl cyclooctatetraene-1,2-dicarboxylate which corresponded to a yield of 20.5 percent based upon the amount of DMAD used.

Photolysis of Dimethyl Acetylenedicarboxylate

in Molten Naphthalene at 95°C

A solution of 307.2 g of naphthalene (2.40 moles) and 20 ml of DMAD (0.160 mole) was prepared by heating the components in a 400 ml beaker on the hot plate. The hot liquid was poured into the quartz cell which was

heated to 100° by passing steam through the water jacket of the cell. The quartz cell was placed in the photolysis apparatus and hot water at 90° supplied by a heating bath was passed through the water jacket. The mercury arc lamp was turned on and maintained a current level of 4.0 amps. The hot water flow through the cell was adjusted so that the temperature of the water at the exit was 95°. The solution was irradiated for four days.

The irradiated solution was poured into a one liter round-bottom flask and the cell was rinsed with chloroform. The solvent was evaporated in vacuo on the rotating evaporator using the water aspirator. A specially constructed dry ice condenser was attached to the rotating evaporator and the unreacted starting materials were removed in vacuo at 0.1 mm while heating the flask at 100°C using the steam bath. The non-volatile residue weighed 19.74 g. This residue was dissolved in 50 ml of chloroform and the solution was poured slowly into three liters of 30°-60° petroleum ether. A flocculent precipitate formed immediately. The precipitate was removed by filtration and weighed 7.03 g. It was not investigated further. The solvent was removed from the filtrate in vacuo to give 12.86 g of petroleum ether-soluble residue. Analysis of the residue by vpc indicated that 0.133 g of dimethyl 2,3-benzobicyclo[2.2.2]octa-triene-5,6-dicarboxylate (0.31 percent), 1.56 g of dimethyl 1-naphthylfumarate (3.61 percent), 0.278 g of dimethyl 1,2-benzocyclooctatetraene-5,6-dicarboxylate (0.64 percent), 1.56 g of dimethyl 3,4-benzotricyclo-[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate (3.61 percent), 0.588 g of dimethyl trans-acenaphthene-1,8-dicarboxylate (1.36 percent), and 0.496 g of unknown adduct (1.15 percent) were formed in the reaction in the yields

indicated based on DMAD used.

The residue was combined with residues from shorter photolysis reactions to give a total weight of 18.99 g which was dissolved in 50 ml of chloroform and placed on a column packed with 1140 g of Brinkman No. 7734 silica gel with packing dimensions of 5.5 cm by 108 cm. The chloroform was eluted with 500 ml of 30°-60° petroleum ether. Elution with four liters of benzene gave 2.40 g of naphthalene and other unknown products. Elution with five percent ethyl ether in benzene in one liter portions per fraction gave two fractions containing a combined weight of 0.300 g of unknown products. The next three fractions weighed 0.336 g, 6.53 g, and 0.563 g and contained all of the 1:1 adducts. The next nine fractions contained only unknown products and weighed a total of 8.29 g. The three fractions containing the 1:1 adducts were combined, dissolved in 25 ml of chloroform, and added to a column containing 560 g of Brinkman No. 7734 silica gel. The chloroform was eluted with 500 ml of 30°-60° petroleum ether. Elution with three liters of one percent ethyl ether in benzene gave 0.027 g of unknown products. Further elution with 500 ml of the same solvent gave a fraction, A, weighing 1.17 g which consisted of eight parts of dimethyl 1-naphthylfumarate, 2.5 parts of dimethyl trans-acenaphthene-1,8-dicarboxylate, and one part of unknown adduct. The amounts of the various products were estimated from the peak heights of the vpc trace. Another 500 ml portion of the same solvent gave 0.86 g of a mixture of 1:1 adducts. Three 300 ml portions of five percent ethyl ether in benzene gave fractions weighing 0.36 g, 0.31 g, and 0.30 g, respectively, which contained mixtures of 1:1 adducts. Another 300 ml of the same solvent gave 0.39 g of a mixture of 7.5 parts of dimethyl 3,4-

benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate, 2.5 parts of dimethyl 1,2-benzocyclooctatetraene-5,6-dicarboxylate, and 1.5 parts of dimethyl 2,3-benzobicyclo[2.2.2]octa-triene-5,6-dicarboxylate, as estimated by peak heights. The final fraction, B, was eluted with 500 ml of the same solvent and weighed 2.59 g. It consisted of 7.5 parts of dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate and one part of dimethyl 1,2-benzocyclooctatetraene-5,6-dicarboxylate, as estimated by peak heights. Fraction A was dissolved in five ml of methanol and cooled to -78° in a dry ice-acetone bath with vigorous stirring to form a slush. The slush was incubated in the freezer for two days and formed cream-colored crystals which were isolated by filtration at 0°. The crystals weighed 0.172 g, melted at 61°-63°, and proved to be dimethyl 1-naphthylfumarate. Fraction B was dissolved in a 1:2 mixture of methylene chloride and 60°-90° petroleum ether and cooled to -78° in a dry ice-acetone bath. Cream-colored crystals weighing 1.11 g were isolated by filtration. The crystals melted at 84°-86° and were recrystallized from five ml of the same solvent to give 0.250 g of white crystals melting at 86.5°-87.0°. This compound was dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate.

A molten solution of 307.5 g of naphthalene (2.40 moles), 20.0 ml of DMAD (0.160 mole), and 5.00 g of benzophenone was placed in the quartz cell and irradiated for 24 hours at 95°C. The starting materials were removed in vacuo on the rotating evaporator to give 14.78 g of residue. Analysis of the residue by vpc indicated that the reaction gave 1.04 percent of dimethyl 1-naphthylfumarate (0.450 g), 1.01 percent of dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate (0.436 g),

0.80 percent dimethyl trans-acenaphthene-1,8-dicarboxylate (0.344 g), and 0.28 percent of unknown product (0.122 g) based upon the amount of DMAD used. No other 1:1 adducts were detected.

Thermal Reactions of Naphthalene
with Dimethyl Acetylenedicarboxylate

A mixture of 40.0 g of naphthalene (0.310 mole) and 20.0 ml of DMAD (0.160 mole) was placed in a heavy walled Pyrex tube of 100 ml capacity which was subsequently sealed. The tube was placed in a hot oil bath at a temperature of 180° to 185°C and heated for 48 hours. The tube was opened and the residue was washed into a flask for removal of the unreacted starting materials. Removal of the starting materials in vacuo at 0.1 mm on the rotating evaporator at 100° gave 30.96 g of residue. The residue was dissolved in three liters of 30°-60° petroleum ether. The resulting precipitate was removed by filtration to yield 13.02 g of insoluble residue. The solvent was removed from the filtrate in vacuo on the rotating evaporator to give 17.62 g of residue. The residue was dissolved in 50 ml of chloroform and chromatographed on 1300 g of Brinkman No. 7734 silica gel using 4000 ml of one percent ethyl ether in benzene as the eluent, followed by 1000 ml of three percent ethyl ether in benzene to give two fractions which contained a total of 7.32 g of 1:1 adduct, dimethyl 2,3-benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate (m.p. 76.0-77.0° from methanol), corresponding to a yield of 17.0 percent based upon the amount of DMAD used. Further elution of the column with 2000 ml of five percent ethyl ether in benzene gave a third fraction weighing 1.91 g. Recrystallization of the fraction from methanol gave 1.26 g of white crystals melting

at 118.5°-119.0°. The pmr spectrum of the compound showed four non-equivalent methoxy groups at 5.73 τ , 6.03 τ , 6.15 τ , and 6.18 τ , respectively, which had equal peak areas. The ultraviolet spectrum indicated one maximum at 277 m μ (ϵ = 15,290). The compound was not identified, but it was apparently a dimer of DMAD.

Anal. Calcd. for $C_{12}H_{12}O_8$: C, 50.70; H, 4.23; mol. wt., 284
 Found: C, 47.86, 47.94; H, 4.52, 4.36; mol. wt., 264, 260
 C, 48.95, 49.12; H, 4.59, 4.68

The above reaction was run again with 35 g of naphthalene, 20 ml of DMAD, and 0.25 g of hydroquinone in a sealed Pyrex tube at 170°-180°C for three days. Removal of the starting material in vacuo yielded 34.25 g of residue. The residue was dissolved in 60 ml of chloroform and poured slowly into two liters of 30°-60° petroleum ether. The insoluble residue weighed 20.10 g. The solvent was removed in vacuo to give 14.02 g of residue which was chromatographed on 650 g of Brinkman No. 7734 silica gel using 2000 ml of benzene as an eluent. The first fraction containing all of the 1:1 adduct, dimethyl 2,3-benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate, weighed 10.71 g, which was a 23.3 percent yield based on DMAD used.

A solution of 153.7 g of naphthalene (1.20 moles) and 10.0 ml of DMAD (0.080 mole) was placed in a 250 ml round-bottomed flask which was stoppered and covered with aluminum foil. The flask was set in a steam bath and heated at 100° for seven days with occasional shaking. The starting materials were removed from the flask in vacuo at 100° and 0.1 mm pressure. The residue remaining in the flask weighed 2.71 g. The residue was dissolved in five ml of chloroform and poured into 300 ml of

30°-60° petroleum ether. The precipitate which formed was removed by filtration. The filtrate was evaporated on the rotary evaporator to give 1.306 g of residue. Analysis of the residue by vpc using the Apiezon L column showed that it contained 0.63 g of 1:1 adduct, dimethyl 2,3-benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate, corresponding to a 5.5 percent yield based upon the amount of DMAD used.

Syntheses

1-Naphthylmaleic Anhydride, Dimethyl 1-Naphthylmaleate, and Dimethyl 1-Naphthylsuccinate

Following the procedure of Denivelle and Razavi,¹⁵ 28.6 g of crude 1-aminonaphthalene (0.200 mole) was added to 100 ml of concentrated hydrochloric acid in a 250 ml beaker. The mixture was heated on the hot plate to 100° with vigorous stirring to break up any lumps of the amine hydrochloride. A 0°-110° thermometer was used as a stirring rod so that the temperature of the mixture could be continuously monitored. In a separate 600 ml beaker, 23.0 g of purified maleic acid (0.200 mole) was dissolved in 130 ml of distilled acetone. To this solution was added 8.5 g of cupric chloride dihydrate (0.050 mole) and the solution was cooled to 0°C. The amine hydrochloride suspension was cooled in an ice-salt bath to -5°C and 14.0 g of sodium nitrite dissolved in 25 ml of water was added from a small dropping funnel with the stem of the funnel kept under the surface of the liquid. The addition of sodium nitrite solution was controlled so that the temperature of the solution did not exceed 5°C. As soon as an ex-

15. L. Denivelle and D. Razavi, Compt. rend., 237, 570 (1953).

cess of nitrous acid was shown to be present (test with starch-iodide paper), the diazonium solution was poured immediately into the cold solution of maleic acid and catalyst. The temperature of the solution increased to 15°-20° and some gas evolution occurred. The mixture was allowed to stand overnight with occasional stirring. The viscous dark mixture was partially dissolved in ether and dilute hydrochloric acid was added to remove any unreacted amine and the copper salts. The ether solution was washed several times with dilute hydrochloric acid. Three 250 ml portions of saturated sodium bicarbonate solution were then used to wash the ether solution. The ether layer was then discarded and the sodium bicarbonate solution was extracted with three 150 ml portions of ether to remove the highly colored diazonium coupling products. The sodium bicarbonate solution was carefully acidified to a pH of two with 50 percent hydrochloric acid. The acid solution was extracted with three 300 ml portions of ether. The ether solutions were combined, washed twice with 150 ml volumes of water, and dried over anhydrous sodium sulfate. The solvent was removed on the rotating evaporator to give 6.51 g of crude 2-(1-naphthyl)-3-chlorosuccinic acid. The yield of acid was 11.7 percent. The crude acid was dissolved in 25 ml of distilled acetic anhydride and the solution was refluxed for three hours. The solvent was removed in vacuo to give 4.92 g of crude 1-naphthylmaleic anhydride, corresponding to a yield of 11.0 percent. The crude anhydride was recrystallized from a 50/50 mixture of benzene and 60°-90° petroleum ether to give 2.92 g of yellow crystals melting at 115.0°-116.0° (reported¹⁵ : 116°). A 1.0 g portion of the anhydride was dissolved in 10 ml of a 10 percent solution of potassium hydroxide in water, acidified to a pH of two with 6 N hydro-

chloric acid and the acid was extracted with three 10 ml portions of ether. The ether solution was evaporated on the steam bath and an excess of diazomethane in ether was added. The ether was evaporated on the steam bath to give 1.10 g of dimethyl 1-naphthylmaleate which was a brown oil. The oil would not crystallize from methanol. A 0.70 g portion of the ester was hydrogenated in ethyl acetate with five percent palladium on charcoal to give 0.667 g of crude dimethyl 1-naphthylsuccinate. The ester was recrystallized twice from methanol to give 0.613 g of white crystals melting at 59.0°-60.0°C.

2-Naphthylmaleic Anhydride, Dimethyl 2-Naphthylmaleate, and Dimethyl 2-Naphthylsuccinate

Using the same procedure of Denivelle and Razavi,¹⁵ as was described in the preceding section, 28.6 g of 2-aminonaphthalene (0.200 mole) was dissolved in 100 ml of concentrated hydrochloric acid and diazotized with 14.0 g of sodium nitrite in 25 ml of water at 0°-5°C. The diazonium solution was added to a cold solution of 23.0 g of maleic acid (0.200 mole) and 8.50 g of cupric chloride dihydrate (0.050 mole) in 130 ml of acetone. The mixture stood overnight with occasional stirring. The reaction mixture was worked up as described previously to give 12.41 g of crude 2-(2-naphthyl)-3-chlorosuccinic acid, corresponding to a yield of 22.3 percent. The acid was dissolved in 60 ml of acetic anhydride and refluxed overnight. The solvent was removed in vacuo on the rotating evaporator to give 9.05 g of crude 2-naphthylmaleic anhydride, which represented a yield of 20.0 percent. The crude anhydride was recrystallized from ethyl acetate twice to give 4.95 g of bright yellow crystals melting at 168.0°-169.0° (reported¹⁵: 168°). A 2.0 g portion of the anhydride was dissolved in 10 ml

of 20 percent potassium hydroxide solution, acidified to a pH of two with 6 N hydrochloric acid, and extracted with three 10 ml portions of ether. The ether solution was evaporated on the steam bath and excess diazomethane in ether was added until no more nitrogen was evolved. The solution was evaporated on the steam bath to give 2.1 g of crude dimethyl 2-naphthylmaleate, melting at 78°-80°C. The ester was recrystallized from methanol to give pink crystals melting at 80.0°-80.5°C. A 0.550 g portion of the ester was hydrogenated in ethyl acetate with five percent palladium on charcoal to give 0.470 g of dimethyl 2-naphthylsuccinate which amounted to 0.355 g and melted at 63.5°-64.0°C after two recrystallizations from methanol (reported¹⁶: 65°C).

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 7.10; H, 5.22

Found: C, 70.80, 70.70; H, 5.14, 5.19

Identification of the Reaction Products

See Table 1 for vpc retention times of all compounds which were subjected to vpc analysis.

Dimethyl 2,3-Benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate

This compound was synthesized by the thermal reaction of naphthalene with DMAD as shown previously. The synthetic sample had identical vpc retention times on both the SE-30 and Apiezon L columns as that of one of the minor products from the photochemical reaction of naphthalene with DMAD at 95° without solvent. The retention times were 13.3 minutes on the SE-30 column and 6.2 minutes on the Apiezon L column under the vpc condi-

16. W. H. Linnel, D. W. Matheson, and D. T. Modi, J. Chem. Soc., 3257 (1953).

Table 1. Vpc Retention Times of All Compounds
Subjected to Vpc Analysis

Compound	Retention Time (min)*	
	SE-30	Apiezon L
Dimethyl 2,3-Benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate	13.3	6.2
Dimethyl 1-Naphthylfumarate	13.7	7.0
Dimethyl 1,2-Benzocyclooctatetraene-5,6-dicarboxylate	13.9	7.5
Dimethyl 3,4-Benzotricyclo[3.3.0.0 ^{2,8}]-octa-3,6-diene-6,7-dicarboxylate	14.2	8.5
Unknown	14.8	9.5
Dimethyl <u>trans</u> -Acenaphthene-1,8-dicarboxylate	15.1	10.5
Dimethyl 1-Naphthylsuccinate	--	8.0
Dimethyl 1-Naphthylmaleate	--	9.3
1-Naphthylmaleic Anhydride	--	8.1
Methanol Adduct of DMAD	5.6	--
Cyclohexane Adducts of DMAD	9.4 & 10.0	--
Dimethyl Cyclooctatetraene-1,2-dicarboxylate	9.8	--
Dimethyl 2-Naphthylmaleate	--	11.8
Dimethyl 2-Naphthylsuccinate	--	10.3
Dimethyl Phthalate	--	1.8
Acenaphthylene	--	6.4**

*Determined under conditions described in Chapter III.

**Determined at 270° under otherwise same conditions as for the other compounds on this column.

tions set forth in Chapter III. All of the experimental work was done on the synthetic samples since the compound was not isolated from the photochemical reactions. The compound was a colorless solid melting at 77.0° to 77.5° after two recrystallizations from methanol. The pmr spectrum showed 6.1 protons in a multiplet in the range of 2.65 τ to 3.16 τ . Two of the protons were vinyl protons in a quartet centered at 3.07 τ with coupling constants of 3.2 cps and 7.4 cps. A quartet centered at 4.78 τ with coupling constants of 3.2 cps and 7.4 cps contained 1.9 protons. A singlet at 6.27 τ contained 6.0 protons. The ultraviolet spectrum of the compound showed maxima at 204 $m\mu$ ($\epsilon = 25,600$), 208 $m\mu$ ($\epsilon = 25,300$), and 238 $m\mu$ ($\epsilon = 16,850$). The infrared spectrum of the compound showed the following bands: 3.26 μ (m), 3.32 μ (m), 3.34 μ (m), 3.40 μ (s), 5.80 μ (vs), 6.14 μ (s), 6.30 μ (m), 6.88 μ (s), 7.10 μ (vs), 7.55 μ (s), 7.70 μ (s), 7.90 μ (vs), 8.10 μ (vs), 8.32 μ (vs), 8.72 μ (s), 9.02 μ (s), 9.50 μ (s), 10.50 μ (m), 14.0 μ (s).

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; mol. wt., 270

Found: C, 71.47, 71.49; H, 5.38, 5.14; mol. wt., 269, 260

Hydrogenation of 0.340 g (0.00126 mole) of the compound (m.p. 76.5° - 77.0°) in 50 ml of ethyl acetate using 0.82 g of catalyst resulted in the absorption of 58.0 ml of hydrogen (STP) which corresponded to 2.05 molar equivalents of hydrogen per mole of compound. Only 0.249 g of the tetrahydro compound was recovered from the hydrogenation mixture. The tetrahydro compound had a melting point of 90.5° to 91.0° after two recrystallizations from methanol. Its pmr spectrum showed 4.2 protons in a singlet at 2.84 τ , 6.0 protons in a singlet at 6.34 τ , 2.2 protons in a multiplet

centered at 6.70 τ , 2.3 protons in a broadened singlet at 7.43 τ , and two sets of 1.8 protons each in multiplets at 7.67 τ to 8.0 τ and 8.6 τ to 8.9 τ . The pmr spectrum was identical to that for exo-dimethyl 2,3-benzobicyclo[2.2.2]octane-5,6-dicarboxylate published by Tori, Takano, and Kitahonoki.¹⁷ Their compound had a melting point of 89.0° to 91.5°.¹⁸

Photolysis of Dimethyl 2,3-Benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate in Methanol and Acetone

A solution of 3.00 g (0.011 mole) of dimethyl 2,3-benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate (m.p. 76.5°-77.0°) in 325 ml of methanol was irradiated for 11 hours in the quartz cell under nitrogen with a Pyrex filter placed between the lamp and the cell. The progress of the reaction was followed by removing a 0.25 ml sample from the cell and injecting a 5.0 μ l sample into the vpc using the Apiezon L column at 290° with a flow rate of 50 ml per minute. The disappearance of the starting material which had a retention time of 6.2 minutes was followed as was the appearance of a different peak at 7.5 minutes. The reaction was halted when the peak height of the starting material was reduced to five percent of the peak height of the original sample. Experience with this reaction showed that longer photolysis times or photolysis without the Pyrex filter reduced the yield of the desired product which had a retention time of 7.5 minutes and gave increasing amounts of two unknown products which had retention times of 8.5 minutes and 9.0 minutes. The solvent was removed in vacuo to give 3.03 g of residue. The residue was dissolved in 15 ml of

17. K. Tori, Y. Takano, and K. Kitahonoki, Ber., 97, 2798 (1964).

18. K. Takeda, K. Kitahonoki, M. Sugiura, and Y. Takano, Ber., 95, 2344 (1962).

hot methanol. A flocculent white precipitate formed which was removed by filtration. The precipitate weighed 0.13 g and was discarded. The solvent was removed from the filtrate to give 2.90 g of residue which was dissolved in 10 ml of hot methanol. The solution was placed in the refrigerator overnight. White crystals, melting at 76.0° to 77.0° and weighing 2.17 g (72.3 percent yield), were isolated from the solution by filtration. This compound was identified below as dimethyl 1,2-benzocyclooctatetraene-5,6-dicarboxylate. Analysis of the 0.71 g of residue from the mother liquor from the crystallization by vpc showed that it contained 0.15 g of starting material, 0.23 g of product, and 0.30 g of two unknown compounds which had retention times of 8.7 minutes and 9.0 minutes compared with 7.5 minutes, for the major product. The total yield of major product was 80.0 percent.

A solution of 0.54 g (2.0 mmole) of dimethyl 2,3-benzobicyclo[2.2.2]-octatriene-5,6-dicarboxylate (m.p. 76.5°-77.0°) in 300 ml of acetone was irradiated in the quartz cell for 2.5 hours under nitrogen using a Pyrex filter. The solvent was removed in vacuo to give 0.535 g of residue. Analysis of the residue by vpc showed that it consisted of three products in a peak-height ratio of 8 : 3 : 6 with retention times of 8.5 minutes, 9.9 minutes, and 10.8 minutes using an Apiezon L column at 250°C and flow rate of 50 ml per minute. Under these same conditions, the retention times of dimethyl 1-naphthylfumarate, dimethyl 2,3-benzocyclooctatetraene-5,6-dicarboxylate, and dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate were 8.3 minutes, 9.3 minutes, and 10.0 minutes, respectively. Analysis of the residue by vpc simultaneously with each of the known compounds showed that the only peak in the residue that corres-

ponded in retention time to a known compound was the peak at 9.9 minutes. This peak was apparently the same as dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]-octa-3,6-diene-5,6-dicarboxylate. The residue was not investigated further.

Dimethyl 1,2-Benzocyclooctatetraene-5,6-dicarboxylate

This compound was synthesized by the photochemical reaction described above. The synthetic sample had retention times under the vpc conditions given in Chapter III of 13.9 minutes and 7.5 minutes on the SE-30 column and the Apiezon L column, respectively, identical to those of one of the minor products from the photolysis of DMAD in molten naphthalene at 95°. The compound was not isolated from the photolysis mixtures and all experimental results were obtained from the synthetic sample. The white crystals had a melting point of 77.0° to 77.5° after a total of three recrystallizations from methanol. The pmr spectrum showed 4.4 protons in the region of 2.70 τ to 3.10 τ , 2.00 protons in a doublet centered at 3.29 τ ($J = 11.3$ cps), 2.05 protons in a doublet centered at 3.89 τ ($J = 11.3$ cps), and 6.0 protons in a singlet at 6.35 τ . The ultraviolet spectrum showed a maximum at 200 m μ ($\epsilon = 30,500$) and shoulders at 230 m μ ($\epsilon = 20,500$) and 270 m μ ($\epsilon = 1,800$). The infrared spectrum showed the following bands: 3.27 μ (m), 3.31 μ (s), 3.38 μ (vs), 3.45 μ (w), 3.53 μ (m), 5.79 μ (vs), 6.13 μ (s), 6.75 μ (m), 6.95 μ (vs), 7.15 μ (w), 7.95 μ (vs), 8.15 μ (s), 8.32 μ (s), 8.51 μ (m), 8.69 μ (vs), 8.85 μ (s), 10.5 μ (w), 10.7 μ (m), and 13.5 μ (s).

Anal. Calcd. for C₁₆H₁₄O₄: C, 71.10; H, 5.22; mol. wt., 270

Found: C, 70.96, 71.24; H, 5.27, 5.41; mol. wt., 262, 274

A 1.13 g (4.2 mmole) portion of the compound (m.p. 76.0°-77.0°) was dissolved in 10 ml of hot 95 percent ethanol. A solution of 1.30 g of

potassium hydroxide in 10 ml of 95 percent ethanol was added to the first solution and the mixture was boiled on the hot plate for 15 minutes. A lustrous salt precipitated which was removed by filtration, washed with ethanol, and dissolved in water. The aqueous solution was acidified with 50 percent hydrochloric acid to a pH of 2. An amorphous yellow acid precipitated which was filtered, washed, and dried to give 0.640 g of acid melting at 200.0°-202.0°C (dec.) (60.4 percent yield). A 0.10 g portion of the acid was treated with diazomethane in ether to give 0.09 g of ester which melted at 76.0° to 77.0° after one recrystallization from methanol. A mixed melting point with an authentic sample of the starting material (m.p. 76.0°-77.0°) had a value of 75.5° to 76.5°. The remainder of the acid was vacuum sublimed at 180° at 20 μ pressure for 24 hours to give an amorphous yellow solid on the cold finger of the sublimation apparatus. The solid was washed from the cold finger with acetone and evaporated to dryness on the steam bath to give 0.510 g of orange-yellow crystals which melted at 196.0° to 197.0°. A 0.400 g portion of the crystals melting at 196.0° to 197.0° was treated with 5.0 ml of acetic anhydride at reflux for six hours. The solvent was removed in vacuo to give 0.387 g of dark brown residue. The residue was recrystallized from an equal mixture of benzene and 60°-90° petroleum ether to give 0.257 g of yellow crystals which melted at 196.0° to 197.0°. Comparison of the infrared spectra of the two compounds indicated that they were the same. A mixed melting point of the two showed no depression of the melting point (196.0°-197.0°). The infrared spectrum of the compound melting at 196.0° to 197.0° showed the following bands: 3.33 μ (m), 5.42 μ (s), 5.55 μ (w), 5.65 μ (vs), 6.07 μ (m), 6.75 μ (w), 7.07 μ (w), 7.95 μ (vs), 8.17 μ (m), 9.80 μ (w)

9.82 μ (w), and 11.0 μ (s). Apparently the vacuum sublimation of the acid converted it into the anhydride. The infrared spectrum was consistent with assigning the structure 1,2-benzocyclooctatetraene-5,6-dicarboxylic anhydride to the compound.

Anal. Calcd. for $C_{14}H_8O_3$: C, 75.00; H, 3.60

Found: C, 75.05, 74.98; H, 3.91, 3.86

Hydrogenation of 0.0627 g (0.232 mmole) of the ester (m.p. 76.0°-77.0°) in 40 ml of ethyl acetate using 0.32 g of catalyst resulted in the absorption of 15.1 ml (STP) of hydrogen which corresponded to 2.88 molar equivalents. The hydrogenated ester weighed 0.064 g, was a colorless liquid, and had a pmr spectrum which showed 4.1 protons in a singlet at 2.92 τ , 6.5 protons in a singlet at 6.38 τ , and 9.4 protons in the range of 6.33 τ to 8.40 τ . The ultraviolet spectrum showed maxima at 209 m μ (ϵ = 9,940), 211 m μ (ϵ = 9,900), 263 m μ (ϵ = 460), and 271 m μ (ϵ = 400).
Dimethyl 3,4-Benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate*

This compound was one of the major components isolated from the photolysis of DMAD in molten naphthalene as described earlier. The colorless crystals melted at 86.7° to 87.0° after a total of two recrystallizations from an equal mixture of 30°-60° petroleum ether and methylene chloride. The pmr spectrum showed 4.1 protons in the range of 2.50 τ to 3.05 τ , 0.95 proton in a doublet centered at 5.81 τ (J = 5.9 cps), 3.0 protons in a singlet at 6.42 τ , 3.0 protons in a singlet at 6.45 τ , 1.95 protons in a complex multiplet in the range of 6.53 τ to 6.86 τ , and 1.00

* Named according to the IUPAC rules reviewed by J. Meinwald and J. K. Crandall, J. Am. Chem. Soc., 88, 1292 (1966).

proton in a complex multiplet at 6.91 τ to 7.25 τ . The ultraviolet spectrum showed a maximum at 200 m μ ($\epsilon = 42,500$), a shoulder at 220 m μ ($\epsilon = 19,650$), and a maximum at 265 m μ ($\epsilon = 4,770$). The infrared spectrum showed the following bands: 3.27 μ (w), 3.30 μ (w), 3.32 μ (w), 3.37 μ (m), 3.52 μ (w), 5.72 μ (vs), 5.87 μ (vs), 6.06 μ (s), 6.86 μ (s), 7.00 μ (s), 7.40 μ (s), 7.70 μ (vs), 7.92 μ (vs), 8.25 μ (vs), 8.50 μ (s), 8.55 μ (s), 8.60 μ (s), 9.08 μ (s), 9.32 μ (s), 9.71 μ (vs), 10.0 μ (m), 10.3 μ (m), 10.5 μ (m), 10.9 μ (w), 11.1 μ (w), 11.8 μ (w), 12.2 μ (s), 12.6 μ (s), 12.8 μ (s), 13.0 μ (s), 13.3 μ (m), 14.3 μ (w), and 15.5 μ (m).

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; mol. wt., 270

Found: C, 71.10, 70.97; H, 5.07, 5.20; mol. wt., 271, 274

Hydrogenation of 0.156 g (0.577 mmole) of the compound (m.p. 86.0°-87.0°) in 50 ml of glacial acetic acid using 1.02 g of catalyst resulted in the uptake of 26.2 ml (STP) of hydrogen which corresponded to 2.03 molar equivalents. Analysis by vpc using the Apiezon L column at 290° with a flow rate of 50 ml per minute of the 0.151 g of hydrogenated compound recovered from the solution showed that a 3:5 mixture of two compounds having retention times of 8.9 minutes and 9.4 minutes compared to 8.5 minutes for the starting material. The hydrogenated mixture was a colorless oil and was not investigated further.

A 0.402 g portion of the ester (m.p. 86.0°-87.0°) was dissolved in 15 ml of methanol and 0.70 g of potassium hydroxide was added. The mixture was heated on the steam bath for 30 minutes. The solvent boiled away on the steam bath leaving a brown mass which was dissolved in 10 ml of water. The solution was acidified to a pH of 2 with 50 percent hydrochloric acid. The acid mixture was extracted with three 10 ml portions

of ether. The ether solution was dried over anhydrous sodium sulfate. The solvent was removed to give 0.377 g of viscous liquid which hardened to a glass. Attempts to crystallize the acid from benzene, chloroform, 95 percent ethanol, methanol, and carbon tetrachloride failed. A 0.100 g portion of the acid was treated with excess diazomethane in ether. The solvent was removed to give 0.106 g of yellow oil. Analysis of the oil by vpc on the Apiezon L column at 290° with a flow rate of 50 ml per minute showed that the mixture consisted of three parts of starting ester with a retention time of 9.0 minutes to one part of an unknown compound of retention time of 9.5 minutes. The acid mixture was not investigated further.

A solution of 0.314 g (0.16 mmole) of ester (m.p. 86.0°-87.0°) and 0.094 g of sodium methoxide (1.74 mmole) in 5 ml of methanol-d₁ was refluxed for 48 hours on the steam bath with moisture excluded by a calcium chloride drying tube. The solvent was removed in vacuo and the residue was taken up in an ether-water mixture. The mixture was acidified with dilute hydrochloric acid and extracted with three 10 ml volumes of ether. The ether solution was dried and the solvent was removed to give 0.305 g of residue. The residue was dissolved in 1.0 ml of deuteriochloroform and the pmr spectrum was run on the solution. The pmr spectrum was unchanged indicating that none of the hydrogen was exchanged under these conditions.

A 0.225 g (0.83 mmole) portion of the ester (m.p. 86.0°-87.0°) was dissolved in 325 ml of methanol and irradiated in the quartz cell under nitrogen for one hour. The solvent was removed in vacuo to give 0.224 g of residue which gave 0.217 g of colorless crystals from 2 ml of methanol at 0°; melting at 86.0° to 87.0°. The melting point of a mixture of product and starting material was 86.5° to 87.0°. The vpc retention times of

both starting material and product were 8.9 minutes on the Apiezon L column at 290°.

A 0.318 g (1.18 mmole) portion of the ester (m.p. 86.0°-87.0°) was dissolved in 20 ml of acetone and poured into a solution of 1.09 g (0.69 mmole) of potassium permanganate in 10 ml of water with 0.1 ml of glacial acetic acid. The mixture was allowed to stand overnight at room temperature. The manganese dioxide formed was removed by filtration and the filter cake was washed with two 10 ml volumes of water and two 10 ml volumes of acetone. The organic solvent and part of the water in the filtrate were removed in vacuo. The aqueous solution was acidified to a pH of 2 with dilute hydrochloric acid. The acidic mixture was extracted with three 40 ml volumes of ether. The ether solution was dried over anhydrous sodium sulfate and the solvent was removed to give 0.150 g of residue. The residue was treated with excess diazomethane in ether to give 0.166 g of residue after removal of the solvent. Analysis of the residue by vpc using the Apiezon L column at 200° with a flow rate of 50 ml per minute showed that it contained 0.125 g of a compound which had the same retention time (5.7 min) as dimethyl phthalate. This weight corresponded to a yield of 54.7 percent. The residue also contained small amounts of unknown compounds which had retention times of 5.6 minutes, 9.8 minutes, and 11.0 minutes on the Apiezon L column at 290° with a flow rate of 50 ml per minute. Under the same conditions, dimethyl phthalate had a retention time of 1.8 minutes.

Dimethyl 1-Naphthylfumarate

This compound was a major product from the photolysis of DMAD in molten naphthalene at 95°C. The compound was isolated from the photolysis

mixture as described previously. The pale yellow crystals had a melting point of 62.0°-63.0° after a total of two recrystallizations from methanol at 0°. The sample sent for analysis had a purity of greater than 98 percent as shown by vpc analysis. The compound had retention times of 13.7 minutes and 7.0 minutes on the SE-30 and Apiezon L columns, respectively, under the conditions described in Chapter III. The compound was very difficult to purify with the major impurity being dimethyl trans-acenaphthene-1,8-dicarboxylate. All of the data except the C, H analysis and molecular weight were obtained on samples of about 95 percent purity. The pmr spectrum showed 7.82 protons in the region of 2.17 τ to 3.0 τ , 3.0 protons in a singlet at 6.52 τ and 3.0 protons in a singlet at 6.80 τ . The ultraviolet spectrum showed a maximum at 223 m μ (ϵ = 63,000), a shoulder at 264 m μ (ϵ = 4,400), maxima at 272 m μ (ϵ = 5,430), and 281 m μ (ϵ = 5,780) and a shoulder at 288 m μ (ϵ = 4,760). The infrared spectrum had the following bands: 3.27 μ (w), 3.33 μ (w), 3.39 μ (m), 3.53 μ (w), 5.75 μ (vs), 6.08 μ (m), 6.30 μ (w), 6.98 μ (s), 7.38 μ (m), 7.95 μ (vs), 8.13 μ (s), 8.60 μ (m), 9.20 μ (m), 9.50 μ (w), 9.80 μ (s), 10.9 μ (w), 11.2 μ (w), 12.7 μ (s), and 14.5 μ (w).

Anal. Calcd. for C₁₆H₁₄O₄: C, 71.10; H, 5.22; mol. wt., 270

Found: C, 71.04, 71.14; H, 5.30, 5.21; mol. wt., 272, 268

A 0.813 g (3.01 mmole) sample of the ester (95.0 percent pure by vpc analysis) was hydrogenated in 50 ml of ethyl acetate using 1.80 g of catalyst. The amount of hydrogen absorbed was 64.5 ml (STP) corresponding to 0.96 molar equivalents. The weight of hydrogenated product recovered was 0.729 g. The dihydro compound was recrystallized twice from 5 ml of methanol to give 0.575 g of white crystals, melting at 60.0° to

60.5°. The pmr spectrum of the compound showed 6.8 protons in the region of 1.82 τ to 2.73 τ , 0.97 proton in a quartet centered at 5.12 τ ($J = 5.4$ cps, 10.0 cps), 3.0 protons in a singlet at 6.45 τ , 3.0 protons in a singlet at 6.47 τ , 0.90 proton in a quartet centered at 6.70 τ ($J = 10.0$ cps, 17.0 cps) and 1.08 proton in a quartet centered at 7.42 τ ($J = 5.4$ cps, 17.0 cps). The infrared spectrum showed the following main bands: 3.39 μ (m), 5.76 μ (vs), 6.98 μ (s), 8.6 μ (vs). The infrared spectrum, mixture melting point (60.0°-60.5°) and vpc retention time (8.0 minutes on the Apiezon L column) at 290° and 50 ml per minute indicated that the dihydro compound was identical with the synthetic sample of dimethyl 1-naphthylsuccinate (m.p. 60.5°-61.0°) described previously.

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92

Found: C, 70.54, 70.31; H, 5.80, 5.83

The vpc retention time of dimethyl 1-naphthylfumarate was 7.0 minutes as compared to 9.3 minutes for dimethyl 1-naphthylmaleate on the Apiezon L column at 290° and 50 ml per minute. Since both compounds give the same product on hydrogenation, the compound of melting point 63°, which was formed from the photolysis of naphthalene and DMAD, was dimethyl 1-naphthylfumarate.

Photolysis of Dimethyl 1-Naphthylfumarate

A solution of 0.800 g (2.93 mmoles) of dimethyl 1-naphthylfumarate (97 percent pure by vpc analysis) in 200 ml of methanol was irradiated at room temperature in the quartz cell under nitrogen for 11 hours using the Pyrex filter. The solvent was removed in vacuo to give 0.794 g of residue. Analysis of the residue by vpc using the Apiezon L column at 290° and 50 ml per minute indicated that the residue contained 0.025 g of

starting material and 0.469 g (59.1 percent yield) of dimethyl trans-acenaphthene-1,8-dicarboxylate. No other compounds were observed on the vpc trace. The residue was dissolved in 5 ml of hot methanol and cooled to give 0.375 g of white crystals melting at 83.5°-84.0°. A mixed melting point with a sample of dimethyl trans-acenaphthene-1,8-dicarboxylate melted at 83.0°-84.0°.

Dimethyl trans-Acenaphthene-1,8-dicarboxylate

This compound is the major product from the photolysis of naphthalene and DMAD in methanol at 65°. The compound has identical retention times (10.5 minutes on the Apeizon L column and 15.1 minutes on the SE-30 column, at the standard conditions described in the general experimental procedure) with one of the minor components from the photolysis of DMAD in molten naphthalene at 95°. The compound was not isolated from the hot-melt reaction mixture, but was isolated in good yield from the photolysis in methanol as described previously. All of the data for the compound were obtained using the material isolated from the methanol photolyses. The compound had a melting point of 84.5°-85.0° after a total of three recrystallizations from methanol. The pmr spectrum showed 5.9 protons in the region of 2.34 τ to 2.86 τ , 1.85 protons in a singlet at 4.95 τ and 6.0 protons in a singlet at 6.33 τ . The ultraviolet spectrum showed maxima at 226 m μ (ϵ = 84,800), 247 m μ (minimum, ϵ = 828), 267 m μ (ϵ = 3,840), 277 m μ (ϵ = 6,480), 287 m μ (ϵ = 7,690), 291 m μ (ϵ = 5,690), 298 m μ (ϵ = 5,150), 304 m μ (ϵ = 1,790), 308 m μ (shoulder, ϵ = 696), 315 m μ (ϵ = 663), and 319 m μ (ϵ = 431). The infrared spectrum had the following bands: 3.28 μ (w), 3.34 μ (w), 3.39 μ (m), 3.55 μ (w), 5.75 μ (vs), 6.24 μ (m),

6.98 μ (s), 7.30 μ (m), 7.92 μ (m), 8.15 μ (s), 8.40 μ (vs), 8.60 μ (vs), 9.80 μ (m), and 10.0 μ (m). Attempted hydrogenation of the compound in ethyl acetate using five percent palladium on charcoal as the catalyst resulted in the absorption of no hydrogen.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; mol. wt., 270

Found: C, 71.02, 71.18; 5.36, 5.46; mol. wt., 270, 266

A 0.270 g (01.0 mmole) sample of the ester (m.p. 83.0°-84.0°) was dissolved in one ml of deuteriochloroform and placed in a pmr tube. The region at 4.95 τ was traced and 0.5 ml of methanol- d_1 was added to the pmr tube. The same region was traced immediately and again after 10 minutes with no change in the spectrum. A 0.05 ml volume of a solution of 0.25 g of sodium methoxide in 0.50 ml of methanol- d_1 was then added to the pmr tube. The spectrum was traced at five minute intervals. After 20 minutes had elapsed, the peak at 4.95 τ had been reduced to eight percent of the original peak area. The other peaks were unchanged.

A 0.615 g (2.28 mmoles) sample of the ester (m.p. 83.0°-84.0°) and 0.392 g (7.25 mmoles) of sodium methoxide were dissolved in eight ml of methanol- d_1 and refluxed on the steam bath for two days with moisture excluded. The solvent was removed in vacuo and the residue was immediately neutralized with five ml of 20 percent deuteriosulfuric acid in deuterium oxide. The aqueous mixture was extracted with three 10 ml volumes of ether and dried over anhydrous sodium sulfate. The solvent was removed on the steam bath to give 0.555 g of residue. Analysis of the residue by vpc using the Apiezon L column at 290° with a flow rate of 50 ml per minute showed that the residue was greater than 98 percent of one compound which had a retention time of 10.5 minutes, identical with that of the starting

material. The residue was dissolved in 5 ml of hot methanol and gave 0.368 gram of crystals melting at 82.0° to 83.0° upon cooling. A mixed melting point with the starting material (m.p. 83.0°-84.0°) had a value of 82.5° to 83.5°. The pmr spectrum showed 0.22 proton at 4.95 τ compared with 4.05 protons at 2.34 τ to 2.86 τ and 6.0 protons at 6.33 τ indicating that the compound was 89 percent deuterated.

A 1.20 g (4.45 mmoles) sample of ester (m.p. 83.0°-84.0°) was dissolved in 15 ml of hot 95 percent ethanol and 2.0 g of potassium hydroxide was added. The mixture was heated on the steam bath for five minutes. The potassium salt which precipitated was filtered and washed with 95 percent ethanol. The salt was dissolved in 10 ml of water and acidified to a pH of 2 with 50 percent hydrochloric acid. The acid was filtered, washed with water, and dried in the oven overnight at 115° to give 1.05 g of acid which melted at 205.0° to 208.0° (dec.). A 0.025 g portion of the acid was treated with excess diazomethane in ether and the solution was analyzed by vpc. Only one compound was formed with a retention time of 10.5 minutes on the Apiezon L column at 290° and a flow rate of 50 ml per minute. This retention time was the same as that of the starting ester.

A 0.968 g (4.00 mmoles) sample of the above acid (m.p. 205.0°-208.0°) was dissolved in 25 ml of dry pyridine and heated to 70° in a hot water bath. To this solution was added 2.00 g (4.40 mmoles) of lead tetraacetate. The evolution of gas lasted about 30 seconds and the solution was heated for five minutes more at 70°. The solvent was removed in vacuo on the rotary evaporator. The temperature of the heating bath was kept at or below 70°. The residue in the flask was treated with 20 ml of 20 percent hydrochloric acid. The insoluble lead salts were removed by

filtration and the filter cake was washed with ether. The aqueous solution was extracted with ether and all of the ether solutions were combined. The ether solution was washed three times with saturated sodium bicarbonate solution. The ether solution was dried over anhydrous sodium sulfate and the solvent was removed at 50° on the rotary evaporator to give 0.239 gram of residue. Analysis of the residue on the Apiezon L column at 270° with a flow rate of 50 ml per minute indicated that 0.126 g (20.7 percent yield) of acenaphthylene (6.2 min retention time) had been formed in the reaction. The residue was chromatographed on 100 g of Brinkman No. 7734 silica gel using 30°-60° petroleum ether as an eluent to give 0.097 of brilliant yellow partly solid residue. The residue was dissolved in 2 ml of 90 percent ethanol and cooled to 0° to give 0.047 g of yellow crystals melting at 90.0° to 91.0°. A mixed melting point with an authentic sample of Aldrich reagent grade acenaphthylene (m.p. 90.5° to 91.3°) gave a melting point of 89.5° to 90.5°. The infrared spectra of both samples were identical and showed the following bands: 3.25 μ (w), 3.36 μ (m), 3.38 μ (m), 6.70 μ (m), 6.75 μ (m), 6.83 μ (w), 7.00 μ (vs), 7.20 μ (m), 8.19 μ (m), 8.29 μ (m), 8.50 μ (w), 8.75 μ (m), and 9.30 μ (s).

A 0.54 g (2.00 mmoles) sample of ester (m.p. 83.0°-84.0°) was dissolved in 5 ml of technical grade benzylamine. The solution was heated at 175° for two hours in an oil bath. The mixture was cooled to room temperature and filtered. The filter cake was washed with cold acetone to give 0.330 g of white needles of the benzylamide which melted at 257.0° to 259.0°. The residue was recrystallized once from acetonitrile to give 0.250 g of white needles melting at 259.0° to 260.0°. A mixed melting point of a 50/50 mixture of the above sample with a benzylamide sample

(m.p. 261.0°-262.0°) prepared by E. Grovenstein, Jr. in unpublished work showed a melting point of 258.0° to 259.0°.

A 0.350 g sample of acid (m.p. 205.0°-208.0°) prepared as described previously, was treated with 10 ml of acetic anhydride at reflux for two days. The solvent was removed in vacuo to give 0.337 g of black tarry residue. Analysis of the residue by vpc using the Apiezon L column at 290° with a flow rate of 50 ml per minute showed nothing on the vpc trace from zero to 25 minutes. Under the same conditions, 1-naphthylmaleic anhydride had a retention time of 8.1 minutes.

Photolysis of Dimethyl 1-Naphthylmaleate

A sample of crude dimethyl 1-naphthylmaleate was prepared by treating the mother liquor from the recrystallization of 1-naphthylmaleate described previously (page 31) with 2.5 ml of concentrated sulfuric acid in 50 ml of dry methanol. The solution was refluxed for six hours. The solvent was removed in vacuo and the acid was neutralized with sodium bicarbonate solution. The mixture was extracted with three 25 ml volumes of ether, dried over anhydrous sodium sulfate, and the solvent removed to give 2.35 g of crude residue. The residue was dissolved in 5 ml of chloroform and placed on 100 g of Brinkman No. 7734 silica gel. The sample was eluted with 500 ml of two percent ethyl ether in benzene to give 2.16 g of brown oil which would not crystallize when dissolved in methanol and placed in the freezer for two days. Analysis of the residue by vpc on the Apiezon L column at 290° and 50 ml per minute indicated that the residue contained approximately 75 percent of dimethyl 1-naphthylmaleate with a retention time of 9.3 minutes and about 20 percent of unreacted anhydride with a retention time of 8.1 minutes.

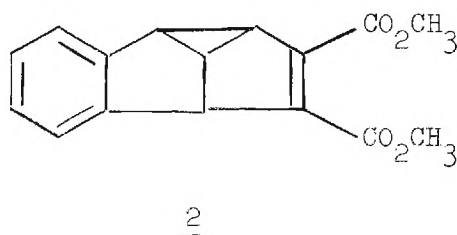
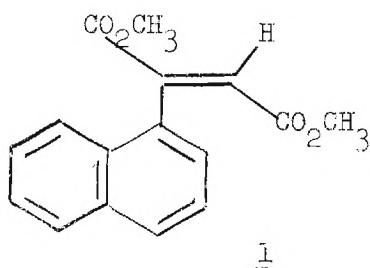
The 2.16 g of residue was dissolved in 275 ml of methanol and irradiated under nitrogen in the quartz cell for eight hours. The solvent was removed in vacuo to give 2.05 g of black residue. The residue was dissolved in 5 ml of chloroform and chromatographed on 100 g of Brinkman No. 7734 silica gel using two percent ethyl ether in benzene as the eluent. The first fraction weighing 0.851 g was eluted with 300 ml of the solvent. Two successive 300 ml volumes of the same solvent gave only a total of 0.025 g of unknown products which were discarded. The first fraction was dissolved in 2 ml of hot methanol and placed in the refrigerator. A white solid, weighing 0.545 (35 percent yield) and melting at 75.0° to 77.0° was isolated by filtration. Recrystallization of the compound from 2 ml of methanol gave 0.210 g of white crystals melting at 80.5° to 81.0°. A third crystallization from 2 ml of methanol gave 0.150 g (9.3 percent yield) of white crystals melting at 82.5° to 83.5°. The compound had a vpc retention time of 10.4 minutes on the Apiezon L column at 290° with a flow rate of 50 ml per minute compared to 10.5 minutes for dimethyl trans-acenaphthene-1,8-dicarboxylate under the same vpc conditions. A mixed melting point of the compound with dimethyl trans-acenaphthene-1,8-dicarboxylate (m.p. 83.0°-84.0°) melted at 82.8° to 83.4°. The infrared, ultraviolet, and pmr spectra of the two compounds were identical.

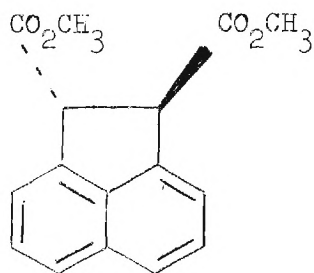
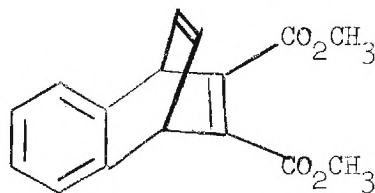
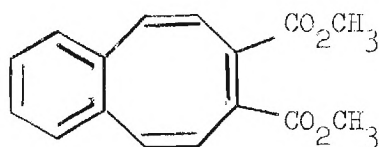
CHAPTER V

DISCUSSION

Photochemical Reactions of Dimethyl Acetylenedicarboxylate
with Naphthalene in Solution

The photochemical reaction of DMAD with naphthalene in dilute solutions was complicated by the reaction of the solvent with DMAD and the low yields of 1:1 photoadducts which made isolation of the products difficult. Much of the non-volatile residue from the reactions consisted of intractable tars which were probably polymers of DMAD. The photochemical reaction of 20.0 g (0.156 mole) of naphthalene with 5.00 ml (0.040 mole) of DMAD in 325 ml of methanol at room temperature for 24 hours yielded, from 10 runs, an average of 1.49 g of non-volatile residue which contained 0.038 g (0.32 percent) of dimethyl 1-naphthylfumarate, 1, 0.011 g (0.10 percent) of dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate, 2, 0.096 g (0.89 percent) of dimethyl trans-acenaphthene-1,8-dicarboxylate, 3, and 0.030 g (0.29 percent) of an unknown compound as determined by vpc analysis. The yield percentages are based upon the amount of DMAD used.



345

Also formed in the reaction was 0.199 g (0.31 percent) of dimethyl 2-hydroxymethylfumarate which resulted from the photochemical addition of methanol to DMAD. The dimethyl 2-hydroxymethylfumarate was identified from its pmr and infrared spectra. The pmr spectrum showed one vinyl proton in a triplet at 3.78 τ ($J = 1.8$ cps), two allylic protons in a doublet at 5.70 τ ($J = 1.8$ cps), and two methoxyl singlets at 6.22 τ and 6.30 τ , respectively. The infrared spectrum had the following characteristic strong absorptions: 2.75 μ to 3.2 μ (broad, hydroxyl), 5.78 μ (carbonyl), and 6.00 μ (double bond). The photochemical addition of methanol to DMAD is similar to the photochemical addition of 2-propanol to acetylenedicarboxylic acid observed by Schenck and Steinmetz.¹⁴ The assignment of the fumaric acid structure to the compound rather than the maleic acid structure was based upon the 1.8 cps coupling constant between the vinyl and

allylic protons. The coupling constant between the vinyl and allylic protons would be expected to be zero if they were on the same side of the double bond.¹⁹ The photolysis of DMAD alone in methanol for 24 hours produced dimethyl 2-hydroxymethylfumarate in 6.5 percent yield based on the amount of DMAD used as determined by vpc analysis. Also produced in the reaction were large quantities of several other unknown products which made separation of the products impossible. The addition of a small amount of naphthalene to the methanol solution did not appreciably change the amounts of products formed by irradiation.

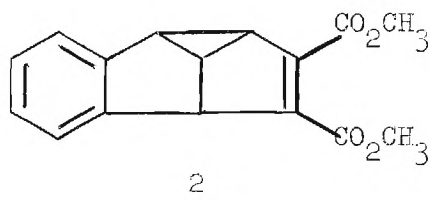
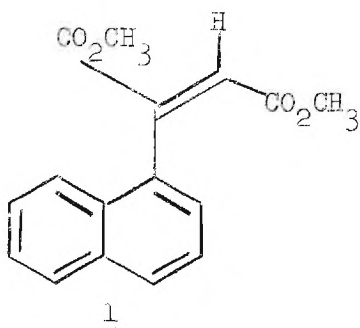
The photochemical reaction of naphthalene with DMAD in cyclohexane resulted in a poor yield of 1:1 adducts. Analysis of the product mixture by vpc indicated that six parts of dimethyl 1-naphthylfumarate, 1, one part of dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate, 2, four parts of dimethyl trans-acenaphthene-1,8-dicarboxylate, 3, and four parts of the unknown 1:1 adduct, estimated from the peak heights. Again the solvent had reacted photochemically with DMAD to produce products which had approximately the correct elemental analysis and molecular weight for 1:1 adducts of cyclohexane and DMAD. These compounds were probably dimethyl cyclohexylfumarate and dimethyl cyclohexylmaleate.

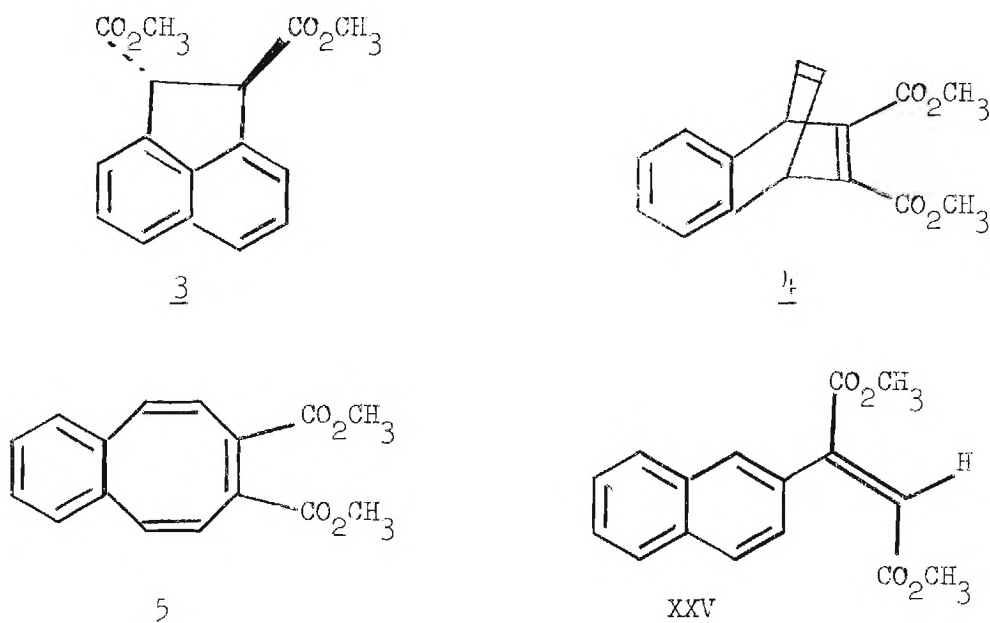
With benzene as solvent, poor yields of the 1:1 photoadducts of naphthalene with DMAD and benzene with DMAD (dimethyl cyclooctatetraene-1,2-dicarboxylate) were obtained. Qualitative vpc analysis using the peak heights indicated that 1.5 parts of 1, 5.4 parts of 2, 2.0 parts of 3, and 1.4 parts of unknown adduct were obtained. With no naphthalene present,

19. J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p. 99.

benzene reacted photochemically with DMAD to give the 1:1 adduct in 20.5 percent yield based on the amount of DMAD used. Apparently naphthalene acted as an inhibitor in the photoreaction of benzene with DMAD.

In order to improve the yield in the photoreaction of naphthalene with DMAD in methanol, the reaction was run at higher concentrations in refluxing solvent. A solution of 60.0 g of naphthalene (0.470 mole) and 20.0 ml of DMAD (0.160 mole) in 275 ml of methanol was irradiated for four days. Analysis by vpc of the residue from the work-up of the reaction indicated that 0.79 percent of dimethyl 1-naphthylfumarate, 1, 0.71 percent of dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-5,6-dicarboxylate, 2, 7.46 percent of dimethyl trans-acenaphthene-1,8-dicarboxylate, 3, and 0.81 percent of unknown adduct were formed in the reaction based upon the amount of DMAD used. Compound 3 was isolated from the reaction in 7.06 percent yield. No more than a total of 0.2 percent of dimethyl 2,3-benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate and dimethyl 1,2-benzocyclo-octatetraene-5,6-dicarboxylate were formed in the reaction.





Photolysis of Dimethyl Acetylenedicarboxylate
in Molten Naphthalene at 95°

The photolysis of DMAD in molten naphthalene at 95° simplified the reaction in that there was no solvent to react with the DMAD in competition with the naphthalene. The yields from the reaction were not very high (about 10 to 12 percent of 1:1 adducts based on the amount of DMAD used) and the higher temperature of the reaction probably increased the thermal polymerization of DMAD. In a typical reaction, 307.5 g of naphthalene (2.40 moles) and 20.0 ml of DMAD (0.160 mole) were irradiated for four days at 95°. The residue from the work-up of the reaction contained according to vpc analysis 0.133 g (0.31 percent) of dimethyl 2,3-benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate, 4, 1.56 g (3.61 percent) of 1, 0.278 g (0.64 percent) of dimethyl 1,2-benzocyclooctatetraene-5,6-dicarboxylate, 5, 1.56 g (3.61 percent) of 2, 0.588 g (1.36 percent) of 3, and 0.496 g (1.15 percent) of an unknown adduct which may have been dimethyl

2-naphthylfumarate, XXV. Only 1 and 2 were actually isolated from the reaction mixture. The other 1:1 adducts were obtained by other means and identified as products from the reaction by admixture to the reaction residue and comparison of vpc retention times on two different columns.

The addition of benzophenone as a photoactivator for the molten naphthalene reaction apparently did not enhance the yield of 1:1 adducts to any noticeable extent.

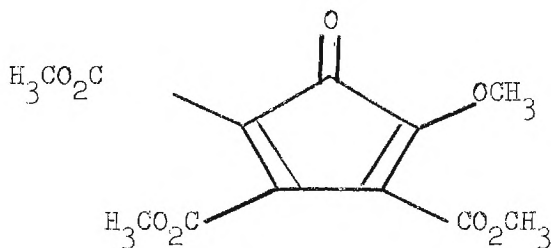
The irradiation of 20 ml (0.160 mole) of DMAD in 307.0 g (2.4 moles) of molten naphthalene at 95° for seven days with the Pyrex filter between the mercury lamp and the quartz cell produced only 2.7 g of non-volatile residue after work-up compared with 12.9 g of residue obtained without the Pyrex filter in four days. Qualitative analysis of the residue by vpc indicated that 0.7 parts of 4, 3.4 parts of 1, 3.2 parts of 5, 3.3 parts of 2, 5.2 parts of 3, and 1.4 parts of unknown 1:1 adduct were formed using the peak heights to determine the relative amounts.

Thermal Reaction of Naphthalene with Dimethyl

Acetylenedicarboxylate

Heating a mixture of naphthalene and DMAD at 180° in a sealed tube gave dimethyl 2,3-benzobicyclo[2.2.2]octatriene-6,7-dicarboxylate, 4, as the major product in 17 to 23 percent yield based on the amount of DMAD used. An unidentified minor product, which was apparently a dimer of DMAD, was also isolated from the reaction mixture. The minor product was unusual in that its pmr spectrum showed only four non-equivalent methoxy groups at 5.73 τ , 6.03 τ , 6.15 τ , and 6.18 τ . The ultraviolet spectrum showed only one maximum at 277 m μ (ϵ = 15,290). The C,H-analysis and mole-

cular weight were approximately correct for $C_{12}H_{12}O_8$. A suggested structure for the compound is XXVI.



XXVI

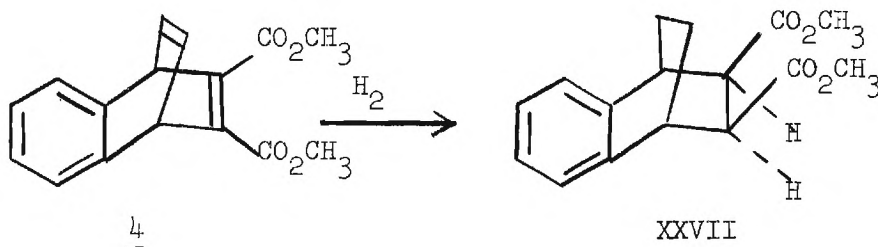
The addition of hydroquinone as an inhibitor improved the yield of the thermal reaction somewhat by raising the yield from 17 percent to 23 percent.

Identification of the Reaction Products

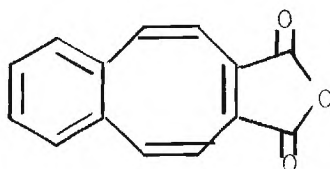
According to the vpc analyses of the various photochemical reactions of naphthalene and DMAD, there were six products formed which had retention times corresponding to 1:1 adducts of the reaction products. Three of the compounds, dimethyl 1-naphthylfumarate, 1, dimethyl 3,4-benzotricyclo-[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate, 2, and dimethyl trans-acenaphthene-1,8-dicarboxylate, 3, were actually isolated from photochemical reaction mixtures; dimethyl 2,3-benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate, 4, was isolated from the thermal reaction of naphthalene and DMAD; and dimethyl 1,2-benzocyclooctatetraene-5,6-dicarboxylate, 5, was synthesized by the photolysis of 4 in methanol. Compounds 4 and 5 were correlated with the 1:1 adducts in the photolysis mixtures by vpc retention times.

The sixth compound was never isolated from the reaction mixture and its structure is unknown.

Compound 4 was isolated from the thermal reaction of naphthalene and DMAD. This compound is expected to have the structure of dimethyl 2,3-benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate by analogy with other Diels-Alder reactions of naphthalene.¹⁸ This structure was confirmed by C,H-analysis and molecular weight determination which agreed with the formula $C_{16}H_{14}O_4$. Moreover, the pmr spectrum showed four aromatic protons in the range of 2.65 τ to 3.16 τ , two vinyl protons in a quartet centered at 3.07 τ ($J = 3.2$ cps, 7.4 cps), two benzylic protons in a quartet centered at 4.78 τ ($J = 3.2$ cps, 7.4 cps), and six protons in a methoxyl singlet at 6.27 τ . The coupling constants were consistent for allylic protons coupled with vinyl protons ($J = 4$ -10 cps).¹⁹ The absorption of the six methoxy protons at the same value indicate that the two carbomethoxy groups are equivalent. Finally, compound 4 absorbed two molar equivalents of hydrogen to give a tetrahydro compound which had a pmr spectrum and melting point identical with those previously reported^{17,18} for compound XXVII.



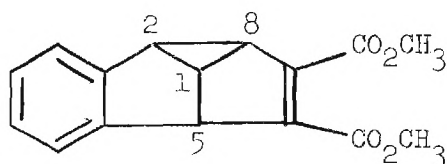
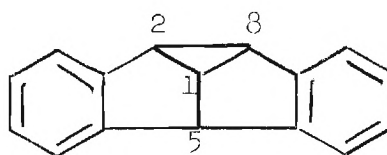
The photolysis of 4 in methanol produced dimethyl 1,2-benzocyclooctatetraene-5,6-dicarboxylate, 5, as the initially formed product. Compound 5 had the correct C,H-analysis and molecular weight for $C_{16}H_{14}O_4$. The pmr spectrum showed four aromatic protons in the region of 2.70 τ to 3.10 τ , two vinyl protons in a doublet centered at 3.29 τ ($J = 11.3$ cps), two vinyl protons in a doublet centered at 3.89 τ ($J = 11.3$ cps), and six methoxyl protons in a singlet at 6.35 τ . The coupling constant between the vinyl protons was consistent with the protons on the double bond being cis ($J = 7-12$ cps).¹⁹ The methoxyl singlet indicates that the carbomethoxyl groups were equivalent. The ultraviolet spectrum is similar to benzocyclooctatetraene²⁰ and dimethyl cyclooctatetraene-1,2-dicarboxylate (see Appendix B). The compound absorbed three molar equivalents of hydrogen; this result was indicative of the benzocyclooctatetraene skeleton. Saponification of 5, followed by vacuum sublimation at 180° of the acid formed, produced a cyclic anhydride, $C_{14}H_8O_3$, (IR: C = O at 5.42 μ and 5.65 μ), evidently 1,2-benzocyclooctatetraene-5,6-dicarboxylic anhydride, XXVIII. This result demonstrated that the two carbomethoxyl groups of 5 are on adjacent carbon atoms. The sum of the evidence available for compound 5 requires that this compound have the structure of dimethyl 1,2-benzocyclooctatetraene-5,6-dicarboxylate.



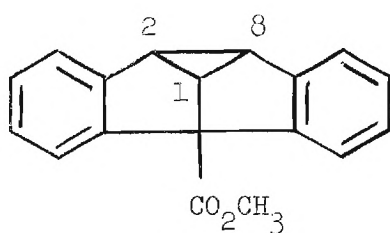
XXVIII

20. G. Wittig, H. Eggers, and P. Duffner, Ann., 619, 10 (1958).

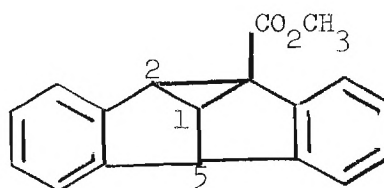
One of the major products from the photolysis of DMAD in molten naphthalene was dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate,2. This compound had the correct molecular weight and elemental analysis for C₁₆H₁₄O₄. The pmr spectrum showed four aromatic protons in the region of 2.50 τ to 3.05 τ , one benzylic proton in a doublet centered at 5.81 τ ($J = 5.9$ cps), two methoxy groups in singlets at 6.42 τ and 6.45 τ , two protons in a complex multiplet at 6.53 τ to 6.86 τ , and one proton in a complex multiplet at 6.91 τ to 7.25 τ .

2

XXIX



XXIII



XXIV

The non-aromatic portion of the pmr spectrum of XXIX is reported²¹ to have one proton in a doublet at 5.68 τ (proton 5), one proton in a

21. G. F. Emerson, L. Watts, and R. Pettit, J. Am. Chem. Soc., 87, 131 (1965).

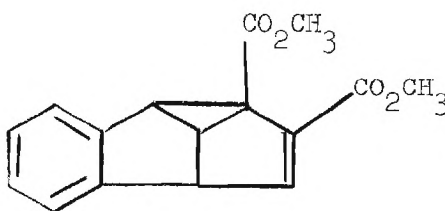
multiplet at 6.47 τ (proton 1), and two protons in a doublet at 7.10 τ (protons 2 and 8). Compound XXIII has the following pmr absorptions for its non-aromatic protons:¹² proton 1, triplet centered at 5.96 τ ($J = 6.5$ cps) and protons 2 and 8, doublet centered at 6.92 τ ($J = 6.5$ cps). Compound XXIV has the following absorptions for its non-aromatic protons:¹² proton 5, doublet centered at 5.50 τ ($J = 5.0$ cps), and protons 1 and 2, multiplet extending from 5.9 τ to 6.1 τ . Using compounds XXIII, XXIV, and XXIX as models, the absorptions of the non-aromatic protons in compound 2 can be assigned with reasonable certainty. Proton 5 is both allylic and benzylic and coupled to only one proton. Thus this proton gave the doublet at 5.81 τ . The proton at position two is benzylic and it probably gave the complex multiplet at 6.91 τ to 7.25 τ analogous to the same protons in XXIX and XXIII which absorbed at 7.10 τ and 6.92 τ , respectively. Protons 1 and 8 produce an overlapping absorption in a complex multiplet at 6.53 τ to 6.86 τ . An attempt at a spin-decoupling study of compound 2 did not give any useful information on the coupling constants of protons 1, 2, and 8. The unusually low absorption for proton 1 in compounds XXIX, XXIII, and XXIV has been explained by the proton lying almost in the plane of the benzene rings where it could be shifted to a lower field by the ring current²² (see reference 21, footnote 14). In compound 2, proton 1 is in the plane of the benzene ring and the double bond. The double bond does not influence the proton as much as the benzene ring so the absorption of proton 1 falls in the region of 6.53 τ to 6.86 τ rather than at 5.9 τ to 6.1 τ as in compounds XXIII and XXIV or

22. Dyer, op. cit., p. 82.

6.43 τ in compound XXIX.

Hydrogenation of compound 2 resulted in the absorption of two molar equivalents of hydrogen, corresponding to the reduction of the double bond and the cyclopropane ring. Reduction of the double bond first followed by reduction of the cyclopropane ring would lead to at least two compounds since two bonds of the cyclopropane ring were benzylic and nearly equally likely to be reduced. Two compounds were in fact obtained upon hydrogenation according to vpc analysis of the product.

Saponification of 2 followed by reesterification of the acid mixture indicated from the vpc analysis of the resultant ester that a minor product of longer retention time had been formed in the reaction. This compound may have been the valence-bond tautomer of 2, XXX. However, the mixture was not separated and there was no evidence supporting the formation of XXX.



XXX

Oxidation of 2 with potassium permanganate in acetone gave dimethyl phthalate as the major product from the reaction along with small amounts of unidentified products. Compound 2 was stable to ultraviolet light as it was recovered unchanged after photolysis for one hour in the quartz

cell in methanol. On the basis of all of the evidence cited, compound 2 likely has the structure of dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]-octa-3,6-diene-5,6-dicarboxylate.

The other major product isolated from the photolysis of DMAD in molten naphthalene was dimethyl 1-naphthylfumarate, 1. This compound had the correct elemental analysis and molecular weight for a 1:1 adduct, C₁₄H₁₆O₄ and was partially identified as a vinyl naphthalene derivative from its spectral characteristics. Hydrogenation of 1 resulted in the absorption of one molar equivalent of hydrogen to form dimethyl 1-naphthylsuccinate, XXXI, which in turn was synthesized by hydrogenation of a known sample of dimethyl 1-naphthylmaleate, XXXII. Compound 1 had a different vpc retention time from that of XXXII. The synthetic route to dimethyl 1-naphthylsuccinate, XXXI, from 1-aminonaphthalene via the Meerwein reaction is depicted in Figure 1. This synthesis had previously been reported¹⁵ only to the stage of 1-naphthylmaleic anhydride.

The pmr spectrum of 1 showed eight protons in the aromatic and conjugated vinyl region of 2.17 τ to 3.0 τ * and two non-equivalent methoxy singlets at 6.52 τ and 6.80 τ . The compound absorbed one molar equivalent of hydrogen to give XXXI which had a pmr spectrum showing seven aromatic protons, two non-equivalent methoxy groups and three protons which exhibited a typical ABC coupling pattern. Proton A on the carbon next to the naphthalene group absorbed in a quartet at 5.12 τ ($J_{AB} = 10.0$ cps, $J_{AC} = 5.4$ cps). Protons B and C were observed as quartets absorbing at 6.70 τ and

* The vinyl protons in diethyl fumarate absorb at 3.17 τ (see Varian NMR Catalogue, No. 213).

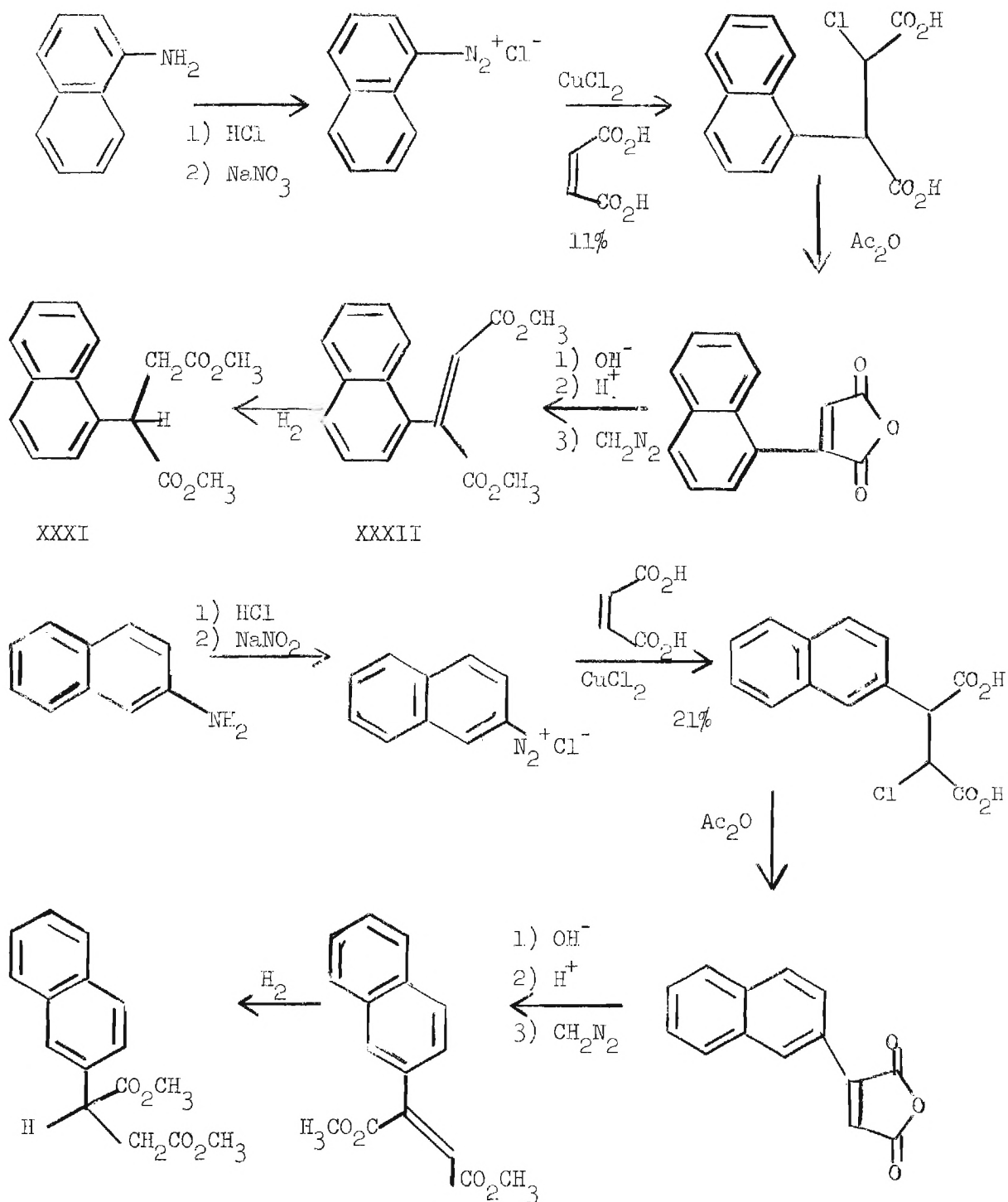


Figure 1. The Syntheses of Dimethyl 1- and 2-Naphthylsuccinate

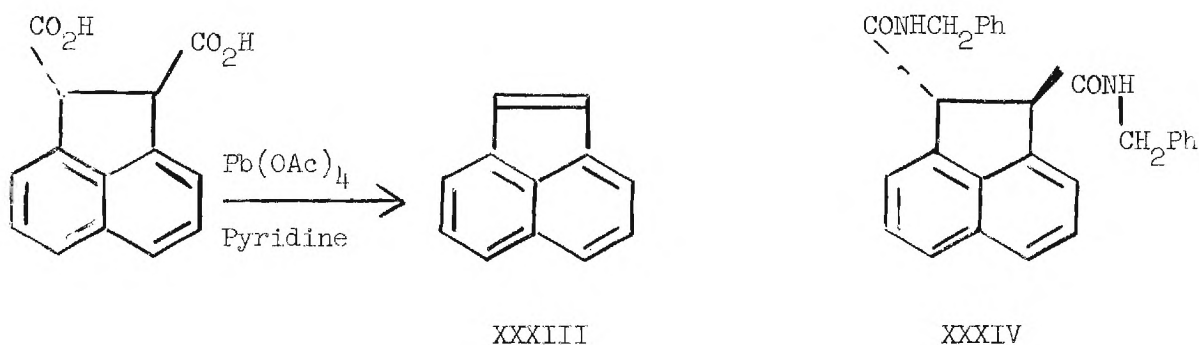
7.42 τ . They were on the same carbon atom and showed a geminal coupling constant of 17.0 cps. Both protons coupled with proton A with $J_{AB} = 10.0$ cps and $J_{AC} = 5.4$ cps. Protons B and C are not equivalent even though there is free rotation about the carbon to carbon bond. This non-equivalence is due to the different electronic environment of the two protons caused by the three different substituents, naphthyl, hydrogen, and carbomethoxy, on the adjacent asymmetric carbon atom.²³

Dimethyl 2-naphthylmaleate and dimethyl 2-naphthylsuccinate were synthesized as shown in Figure 1. Dimethyl 2-naphthylmaleate had a different vpc retention time (see Table 1) from any of the products formed in the photolysis of naphthalene and DMAD. Dimethyl 2-naphthylsuccinate was shown to be different from XXXI, the product formed by hydrogenation of 1, by vpc retention time.

The major product from the photolysis of naphthalene and DMAD in refluxing methanol was dimethyl trans-acenaphthene-1,8-dicarboxylate, 3. This compound was also formed from the photolysis of dimethyl 1-naphthylfumarate, 1, and dimethyl 1-naphthylmaleate, XXXII, in methanol. Compound 3 had the correct elemental analysis and molecular weight for $C_{16}H_{14}O_4$. The pmr spectrum of 3 showed six aromatic protons at 2.34 τ to 2.86 τ , two benzyl protons in a singlet at 4.95 τ , and six methoxy protons in a singlet at 6.33 τ . The two benzylic protons were readily exchanged for deuterium using sodium methoxide in methanol- d_1 . This ready exchange implies that both protons are on carbon atoms adjacent to carbomethoxy groups.

23. Ibid., p. 120.

Compound 3 was saponified to an acid which was oxidized with lead tetraacetate²⁴ in 20 percent yield to a product which was shown to be identical to a known sample of acenaphthylene, XXXIII. The formation of XXXIII establishes the carbon skeleton of the molecule.

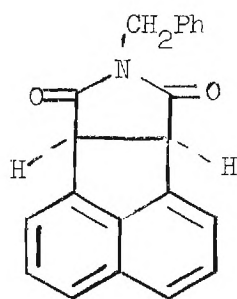


A benzylamide derivative was made by reacting 3 with benzylamine to form the dibenzylamide, XXXIV. Compound XXXIV was identical with a dibenzylamide isolated by E. Grovenstein, Jr.²⁵ This dibenzylamide had been isolated from a reaction mixture from the photolysis of naphthalene and DMAD in methanol after treatment with benzylamine. In this early work, an attempt was made to cyclize the dibenzylamide in trifluoroacetic acid to the imide, XXXV. This attempt was not successful under the conditions which successfully formed the imide, XXXVI, from the dibenzylamide, XXXVII, made from dimethyl naphthalene-2,3-dicarboxylate. This failure to form the imide, XL, indicated that the two carbomethoxy groups are trans to each other.

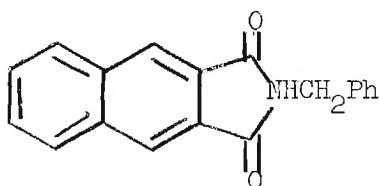
24. L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley and Sons, Inc., New York (1967), pp. 556-557.

25. E. Grovenstein, Jr., unpublished work.

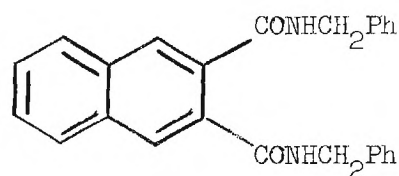
An attempt at formation of a cyclic anhydride from the acid made by saponification of 3 was not successful. This fact also supports the trans arrangement of the carbomethoxy groups.



XXXV



XXXVI



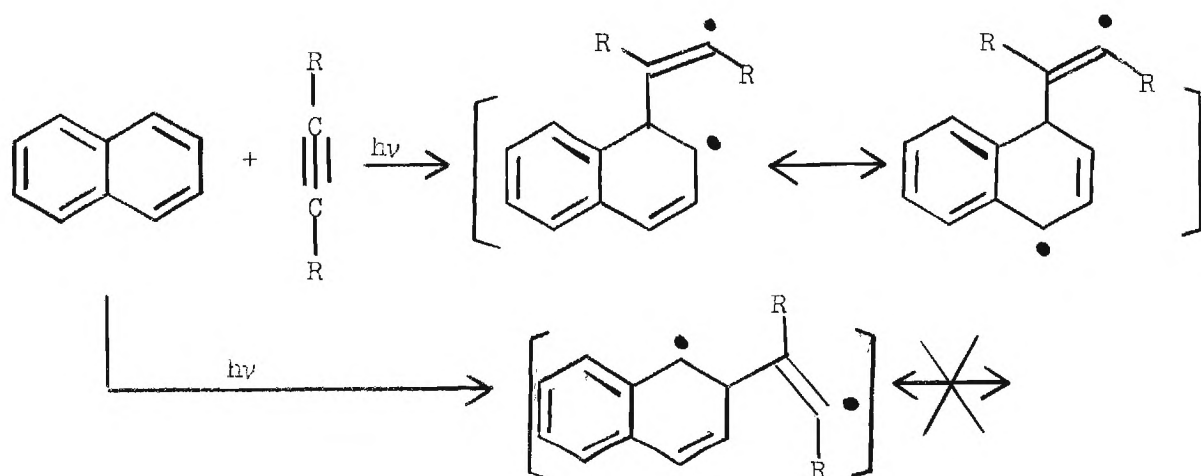
XXXVII

Mechanistic Considerations

The photochemical reactions of acetylene derivatives with aromatic compounds have produced different types of compounds as noted in earlier works^{3,4,5,8,10} and in this research. The initial step in the reaction might be the formation of a complex between the molecules, followed by excitation of the complex to the triplet state. The excited triplet could then collapse into a 1,2-cycloadduct. This mechanism had been suggested for the photochemical reaction of benzene and maleic anhydride.²⁶ The photochemical reactions of benzene with DMAD,^{3,4} benzonitrile with alkylacetylenes,⁵ and diphenylacetylene with naphthalene¹⁰ could fall in this category since the products were postulated to have been formed from 1,2-cycloadducts as intermediates. Alternately, the initial step in the re-

26. W. M. Hardman and G. S. Hammond, J. Am. Chem. Soc., 89, 3200 (1967).

action could involve the excitation of the naphthalene to an electronically excited state, which would probably be ultimately a triplet state, followed by attack of the excited molecule on the acetylene moiety. The molecules are bonded at the 1-position of the naphthalene rather than at the 2-position due to the greater resonance stability of the diradical formed at the 1-position as illustrated. This greater stability of the diradical at the 1-position may explain why no compounds were isolated from the reaction mixtures which could have been formed only from attack at the 2-position.

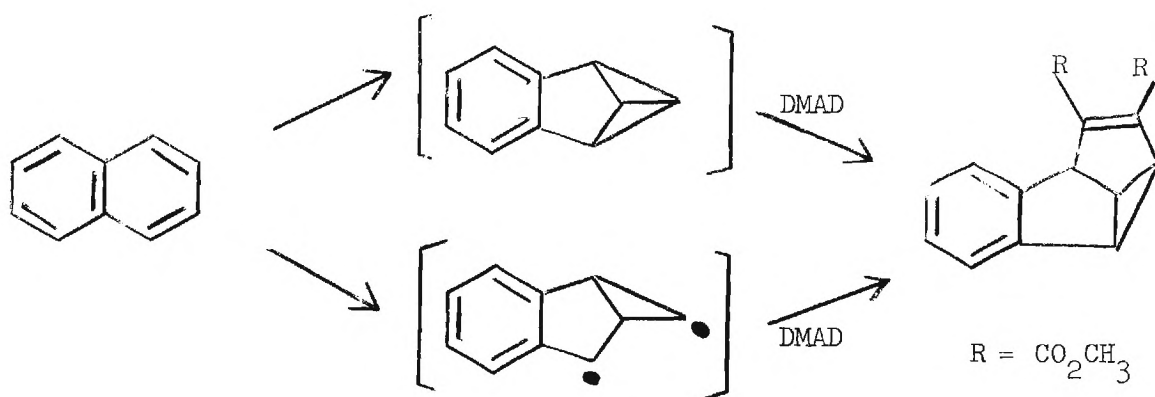


Once the initial attack had formed a carbon to carbon bond, the unbonded radical would be free to react in at least three ways. The unbonded radical could attack the adjacent carbon to give a 1,2-adduct,^{1-6,10} attack the carbon atom diagonally across the ring to give the 1,3-adduct,^{7,8} or undergo a 1,3-hydride shift to give a vinyl derivative of the aromatic compound. All of these pathways have apparently been utilized in various photochemical reactions of acetylenes with aromatic compounds as illustra-

ted in Figure 2.

Concerted 1,2- and 1,3-cycloaddition of the acetylene to the aromatic ring could explain most of the products obtained, but it is unlikely that there would be direct insertion of the acetylene into a carbon-hydrogen bond to form a vinyl derivative (no related reaction is known). Thus, initial attack to form a single carbon to carbon bond between the acetylene and the aromatic ring seems likely, at least for the formation of dimethyl 1-naphthylfumarate,1.

Concerted 1,3-addition of DMAD to naphthalene could proceed by the excitation of the naphthalene to the naphthalene analogue of benzvalene⁷ or via the formation of the diradical shown below.⁸ The reactive intermediate could then react in a concerted Diels-Alder fashion with DMAD to



give compound 2. If the reaction proceeds through this path, the "naphthalene" intermediate appears to be more likely than the diradical intermediate, analogous to the 1,3-addition of alcohols to benzene.²⁷ Regard-

²⁷. L. Kaplan, J. S. Ritscher, and K. E. Wilzbach, J. Am. Chem. Soc., 88, 2281 (1966).

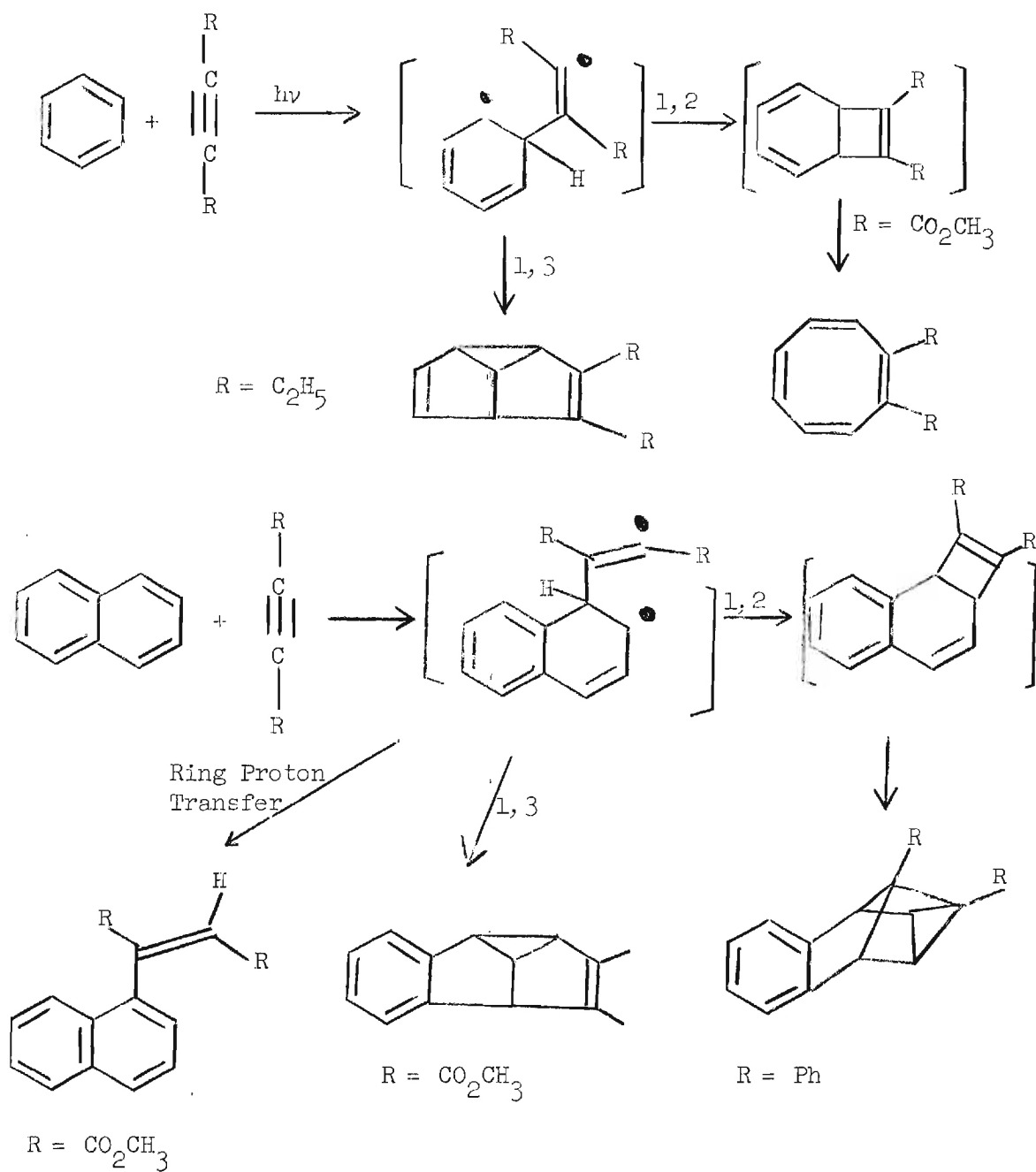


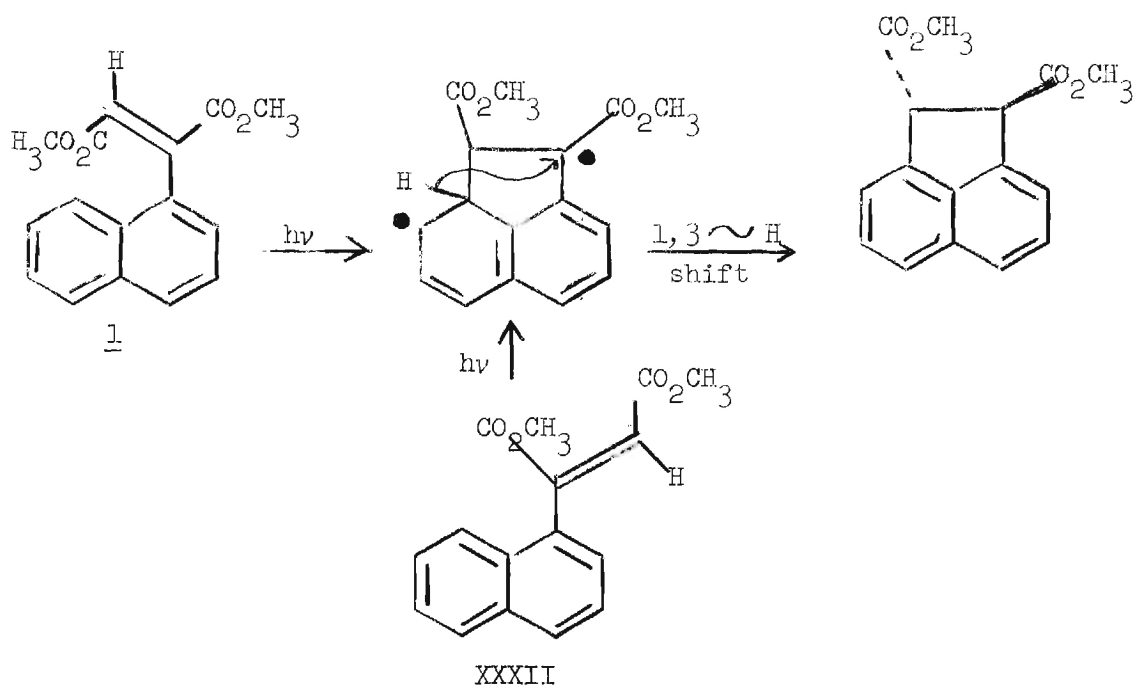
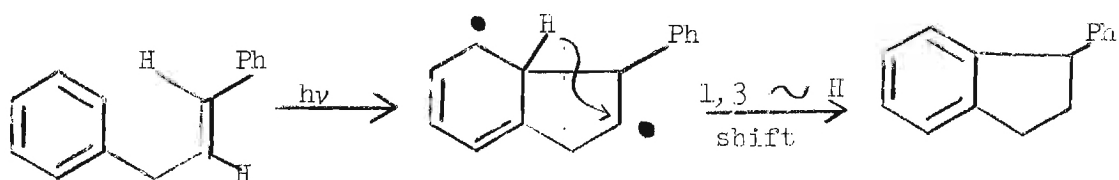
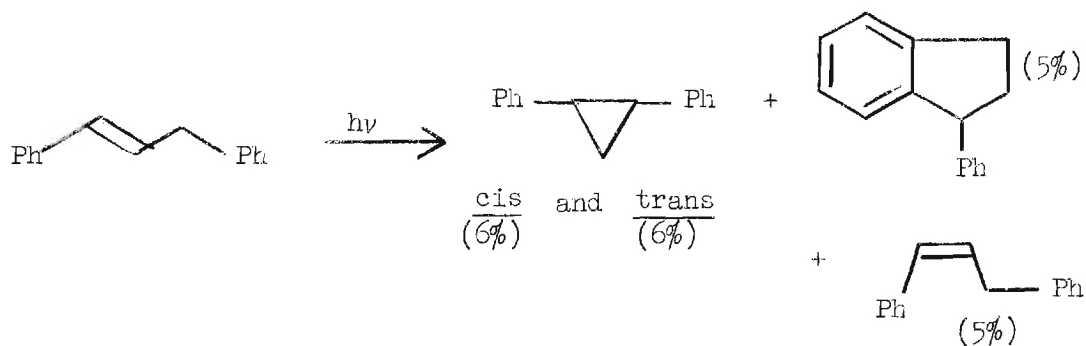
Figure 2. Examples of Two Stage Photochemical Reactions

less of the excited intermediate, relatively more 2 is formed when benzene and molten naphthalene are used as solvents for the photochemical reaction than when methanol or cyclohexane is the solvent. This fact somewhat supports a concerted 1,3-addition over the two-step addition via the diradical intermediate shown in Figure 2, since the solvent can absorb the light and be activated more readily when there is no inert solvent present to deactivate the molecules by collision.

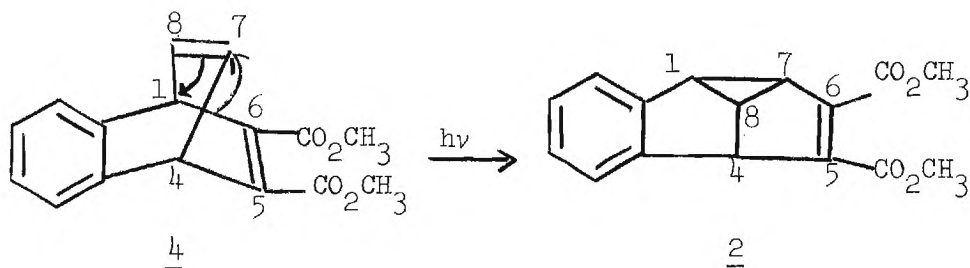
Dimethyl 1-naphthylfumarate, 1, and dimethyl 1-naphthylmaleate, XXXII, were converted into dimethyl trans-acenaphthene-1,8-dicarboxylate, 3, by irradiation in methanol. This transformation also occurred with 1 formed in the photochemical reactions of naphthalene with DMAD, especially in refluxing methanol where 3 was the major product formed in the reaction. In molten naphthalene 1 was a major product and a lesser amount of 3 was produced. Apparently the greater amount of naphthalene present in the molten naphthalene reaction acted as a filter for the ultraviolet light and inhibited the formation of 3. In methanol solution, the solvent may assist in the proton transfer or transfers which must occur in the formation of 3 from 1 or XXXI, but the reaction also occurs in molten naphthalene so the transfer is probably intermolecular. The mechanism of the reaction is not known, but it is analogous to the formation of 1-phenylindane as one of the products from the prolonged irradiation of trans-1,3-diphenylpropene in benzene.²⁸ The formation of 1-phenylindane from trans-1,3-diphenylpropene required a 1,3-proton transfer of the benzene ring

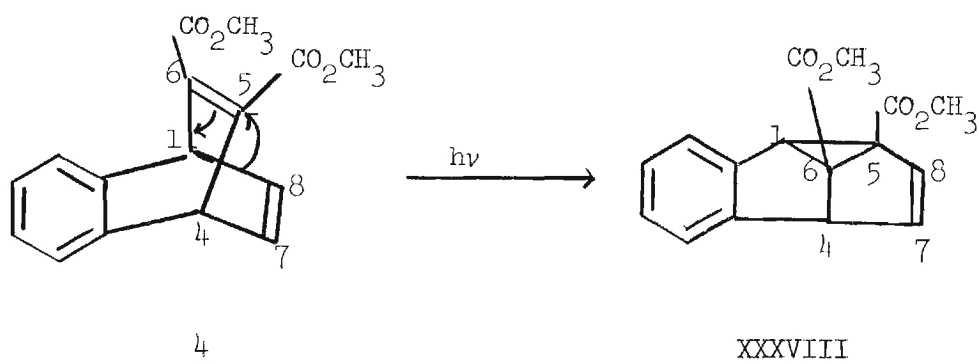
28. G. W. Giffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, J. Am. Chem. Soc., 87, 1410 (1965).

proton. The formation of 3 from 1 and XXXII also required a 1,3-proton transfer of the ring proton.

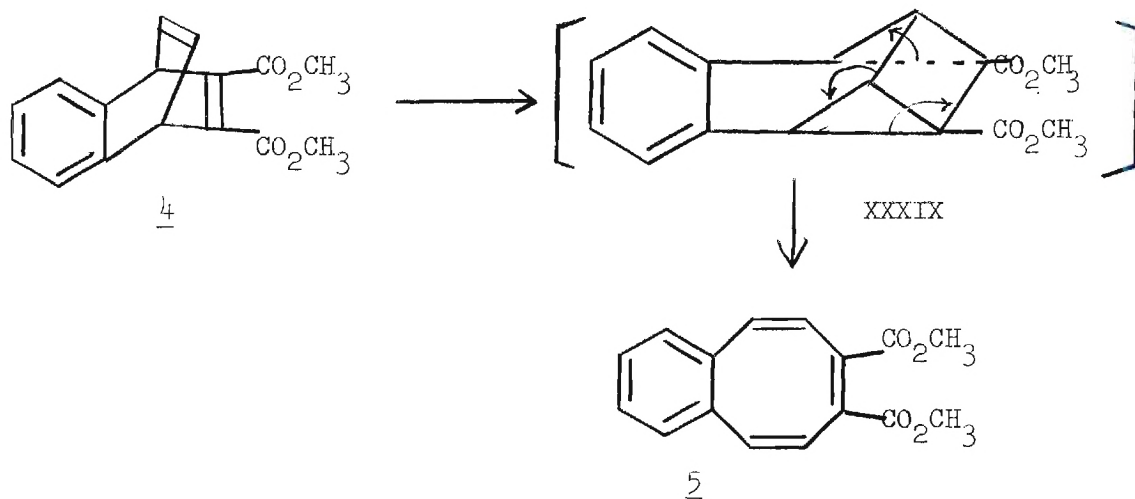


The formation of dimethyl 1,2-benzocyclooctatetraene-5,6-dicarboxylate, 5, as the initial product from the photolysis of dimethyl 2,3-benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate, 4, in methanol presented an interesting transformation from the bicyclo[2.2.2]octatriene system to a cyclooctatetraene system. In contrast, the photolysis of bicyclo[2.2.2]octatriene, XX, yielded mainly tricyclo[3.3.0.0^{2,8}]octa-3,6-diene, XXI, and only a minor amount of cyclooctatetraene.¹¹ Similarly, the photolysis of dibenzobicyclo[2.2.2]octatrienes yielded dibenzotricyclo[3.3.0.0^{2,8}]octadienes only.¹² From 4, two benzotricyclo[3.3.0.0^{2,8}]octa-3,6-dienes, 2 and XXXVIII could be formed by photolysis as well as the benzocyclooctatetraene derivative, 5. The two products, 2 and XXXVIII, may have been present in the reaction mixture since there were two unidentified minor products of longer vpc retention time formed, one of which had the same retention time as 2. The other compound was different in retention time from any of the photolysis products which were identified in the course of this research. Photolysis of 4 in acetone produced still another unidentified compound different in retention time from any of the previously mentioned products along with the two minor products mentioned above; however, no 5 was detected in this reaction mixture by vpc analysis.





The mode of formation of 5 from 4 probably involved an initial formation of a quadricyclic intermediate,²⁹ XXXIX, followed by ring opening to 5.



In order to test whether compound 4 was formed by a thermal reaction at 95° in molten naphthalene, DMAD and naphthalene (in the same proportions

29. S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, 80, 1950 (1958).

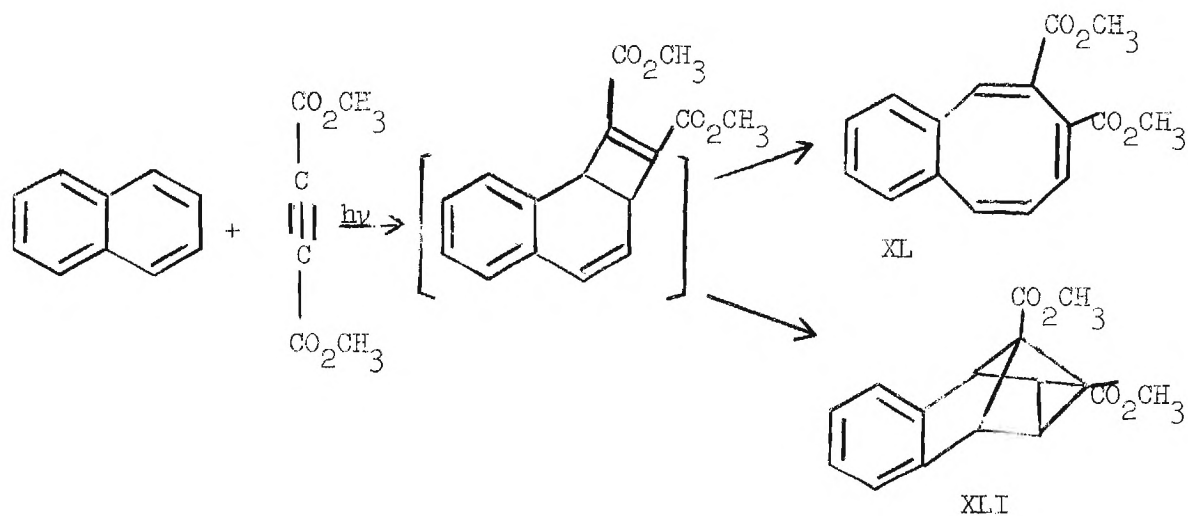
used in the hot-melt photochemical reactions) were heated in the dark at 100° for seven days. A total of 1.26 g of 4 was formed in this reaction compared with a total of 0.41 g of 4 and 5 formed in the photoreaction in four days. Thus, the thermal reaction apparently produces all of 4 which is formed and subsequently partially converted into 5 by photolysis. The possibility that compound 2 is formed photochemically from 4 in the molten naphthalene reactions is mostly precluded by the fact that 2 is formed as a major product in the reactions of naphthalene with DMAD in various solvents at room temperature where only traces of 4 and 5 were detected, if any at all.

Conclusions

It has been found that the photochemical reactions of DMAD with naphthalene under various conditions of solvent and temperature resulted in four or six 1:1 adducts of naphthalene with DMAD. Five of the adducts were identified as dimethyl 1-naphthylfumarate, 1, dimethyl 3,4-benzotri-cyclo[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate, 2, dimethyl trans-acenaphthene-1,8-dicarboxylate, 3, dimethyl 2,3-benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate, 4, and dimethyl 1,2-benzocyclooctatetraene-5,6-dicarboxylate, 5; the sixth adduct was not isolated or identified. Photolysis of DMAD in molten naphthalene at 95° gave 1 and 2 as the major products with 3 as a minor product. Smaller amounts of 4 and 5 were also formed in the reaction. Photolysis of DMAD and naphthalene in methanol at room temperature and at reflux produced 3 as the major product with lesser amounts of 1 and 2 being formed. The solvent also reacted photochemically with DMAD when methanol, cyclohexane, and benzene were used as solvents in

the reaction. The yields of 1:1 adducts were lower when dilute solutions of naphthalene and DMAD were irradiated in such solvents.

The products formed in the photochemical reactions of DMAD with naphthalene were different from what would have been predicted from previous work in the field. No products resulting from a 1,2-cycloaddition reaction followed by ring opening to form XL or from a 1,2-cycloaddition followed by an internal dimerization to form XLI were isolated.



The formation of dimethyl 1-naphthylfumarate, 1, from the photolysis of naphthalene and DMAD is a new type of photochemical reaction which has not been observed previously. The facile photochemical ring closure reactions of 1 and dimethyl 1-naphthylmaleate product, 3, in good yield are an unusual modification of a ring closure reaction reported previously.²⁷

The photolysis of the thermal adduct, dimethyl 2,3-benzobicyclo-[2.2.2]octatriene-5,6-dicarboxylate, 4, in methanol gave dimethyl 1,2-

benzocyclooctatetraene-5,6-dicarboxylate, 5, as the initial major product along with two unidentified minor products which might have been 2 and XXXVIII. This result was different from what would have been predicted from previous work on the photolysis of compounds with the bicyclo[2.2.2]-octatriene skeleton.^{11,12} In contrast, photolysis of 4 in acetone gave a compound different from 5, which was not identified, along with two other products which were probably the same as the minor products formed in the photolysis of 4 in methanol.

No compound corresponding to dimethyl 2-naphthylfumarate was isolated from the photolysis of DMAD and naphthalene. This compound may have been the unidentified 1:1 adduct which was never isolated.

The photochemical reaction of naphthalene with DMAD apparently proceeded preferentially through a two step process involving initial attack of the electronically excited naphthalene on the acetylene derivative to form a carbon to carbon bond at the 1-position. This initial step was followed by a 1,3-proton transfer to give dimethyl 1-naphthylfumarate, 1, as one of the major products which in turn was converted into dimethyl trans-acenaphthene-1,8-dicarboxylate, 3, by a subsequent photochemical reaction. The relative amounts of 1 and 3 produced depended upon whether the reaction was run in molten naphthalene or in refluxing methanol. In molten naphthalene, 1 was one of the major products while in refluxing methanol, 3 was the only major product.

The other major product from the photochemical reaction of DMAD in molten naphthalene was dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate, 2, which could have been formed by two different photochemical pathways. It could have been formed by a direct 1,3-

addition of DMAD to an electronically excited "naphthvalene" intermediate or via a two-step reaction pathway involving formation of a diradical intermediate followed by ring closure diagonally across the ring to give the product.

CHAPTER VI

RECOMMENDATIONS

The photolysis of 1-naphthylmaleic anhydride should be attempted to see if a molecule forced to remain in the cis-configuration would cyclize to form the cis-acenaphthene-1,8-dicarboxylic anhydride. Also, the photolysis of dimethyl 2-naphthylmaleate or 2-naphthylmaleic anhydride should be attempted to see if four-membered ring derivatives could be formed. It would also be interesting to photolyze methyl 4-phenyl-2-butynoate to see if it would form an indene derivative.

The photolysis of dimethyl 2,3-benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate in acetone should be investigated further since this reaction gave a product different from the same reaction in methanol. It also might be possible to change the photolysis conditions in such a manner that the minor products could be isolated and identified. Along with this work, the thermal reaction of naphthalene with methyl propiolate would give a 1,4-adduct which would give several interesting products on photolysis in methanol and acetone.

APPENDICES

APPENDIX A

SOLVENTS USED IN OBTAINING SPECTRA

All ultraviolet spectra were determined in 95 percent ethanol using a one cm cell. All infrared spectra were determined as five percent solutions in carbon tetrachloride or in potassium bromide pellets. All pmr spectra were determined using deuteriochloroform or carbon tetrachloride as solvents with tetramethylsilane added as an internal standard. The pmr values given for the 1:1 adducts were obtained from spectra run in carbon tetrachloride with TMS as an internal standard.

APPENDIX B

ULTRAVIOLET SPECTRAL COMPARISONS OF BENZOCYCLOOCTATETRAENE (A),
 DIMETHYL CYCLOOCTATETRAENE-1,2-DICARBOXYLATE (B),
 DIMETHYL 1,2-BENZOCYCLOOCTATETRAENE-5,6-DICARBOXYLATE (C),
 AND DIMETHYL ACETYLENEDICARBOXYLATE (D)

Wavelength mμ	ε			
	A*	B	C	D
200	--	18,000	20,000	5,560 (max)
210	--	15,300	33,000	3,680
220	22,600	11,650	42,000	2,390
224	--	--	63,500 (max)	--
230	22,800	13,200 (max)	56,500	550
240	28,200 (max)	10,200	10,700	300
250	11,200	5,300	4,150	200
260	5,600	3,000	4,200	108
270	1,850	1,840	5,650	48
280	1,100	1,170	7,100 (max)	24
290	980	730	4,850	12
300	--	615	2,200	0
320	--	480	1,150	0
340	--	270	930	0
360	--	100	550	0
380	--	31	120	0
400	--	--	50	0
* Reference 20				

APPENDIX C

PHOTOLYSIS OF DIMETHYL ACETYLENEDICARBOXYLATE IN METHANOL

To 300 ml of methanol was added 5.0 ml (0.040 mole) of DMAD. The solution was irradiated at room temperature under nitrogen in the quartz cell for 24 hours. The solvent was removed in vacuo to give 7.11 g of viscous yellow residue. Analysis of the residue by vpc using the SE-30 column operated under the conditions described in Chapter III showed that the residue contained 6.5 percent of dimethyl 2-hydroxymethylfumarate which had a retention time of 5.6 minutes. The vpc trace showed that several unknown compounds were present in the residue. The amount of each unknown in the residue was estimated from the peak area (on the assumption of equal peak area per mole as for dimethyl 2-hydroxymethylfumarate). The retention times and amounts of the unknown compounds were as follows: 2.0 min, 3.7 percent; 4.0 min, 9.1 percent; 4.5 min, 4.0 percent, 5.6 min, 6.5 percent (dimethyl 2-hydroxymethylfumarate); 6.4 min, 5.5 percent, 6.6 min, 5.5 percent; 7.2 min, 1.8 percent; and 8.0 min, 2.7 percent. The photolysis of DMAD in methanol would not be a good method for the synthesis of dimethyl 2-hydroxymethylfumarate due to the difficulty of separation from the other products formed.

APPENDIX D

PHOTOLYSIS OF DIMETHYL ACETYLENEDICARBOXYLATE IN MOLTEN

NAPHTHALENE AT 95° USING A PYREX FILTER

A solution of 307.5 g (2.40 moles) of naphthalene and 20.0 ml (0.160 mole) of DMAD was irradiated in the quartz cell at 95° for seven days with a Pyrex filter placed between the lamp and the cell. The starting materials were removed in vacuo to give 10.70 g of residue. The residue was worked up as described previously to give 2.70 g of petroleum ether soluble residue and 7.98 g of insoluble residue. Analysis of the soluble residue by vpc using the SE-30 column under the conditions described in Chapter III indicated that the following relative amounts of 1:1 adducts were present: 0.7 part of dimethyl 2,3-benzobicyclo[2.2.2]-octatriene-5,6-dicarboxylate, 3.3 parts of dimethyl 1-naphthylfumarate, 3.2 parts of dimethyl 1,2-benzocyclooctatetraene-5,6-dicarboxylate, 3.3 parts of dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-6,7-dicarboxylate, 5.2 parts of dimethyl trans-acenaphthene-1,8-dicarboxylate, and 1.4 parts of usual unknown adduct. The relative amounts were estimated from the peak heights of the compounds.

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VITA

Thomas Cooper Campbell, the son of Mr. and Mrs. Thomas T. Campbell, was born February 29, 1932, in Decatur, Illinois. From 1932, he resided in Decatur, Illinois, and attended public schools until his graduation from Decatur High School in June, 1950. He entered Millikin University in September of 1950 and attended Millikin until June of 1952. From September of 1952 until March of 1954, he attended the University of Washington, Seattle, Washington. In May of 1954, he entered the United States Army and served until released in April of 1956. He reentered Millikin University in September of 1956 and graduated with a B.S. in chemistry in June, 1957. He accepted a position as development chemist with the A. E. Staley Manufacturing Company, Decatur, Illinois, until August of 1960. He entered the graduate school of Emory University in September of 1960 and graduated with an M.S. in chemistry in August, 1963. He entered the graduate school of the Georgia Institute of Technology in September of 1963 and completed requirements for the degree of Doctor of Philosophy in chemistry in September, 1967. He is a member of Sigma Xi and the American Chemical Society.

On June 9, 1957, he married the former Elizabeth Ann Le Marr of Decatur, Illinois. He has accepted a position with the Inorganic Chemicals Division of Monsanto Company at St. Louis, Missouri.